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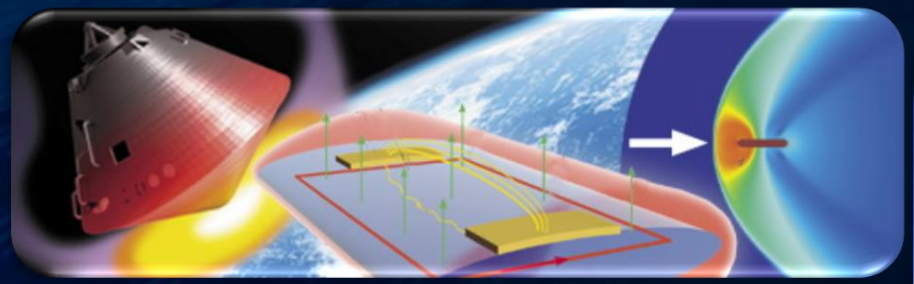


XXXVI International Conference
on Interaction of Intense Energy Fluxes with Matter
ELBRUS 2021
Elbrus, Kabardino-Balkaria, Russia, March 1-6, 2021

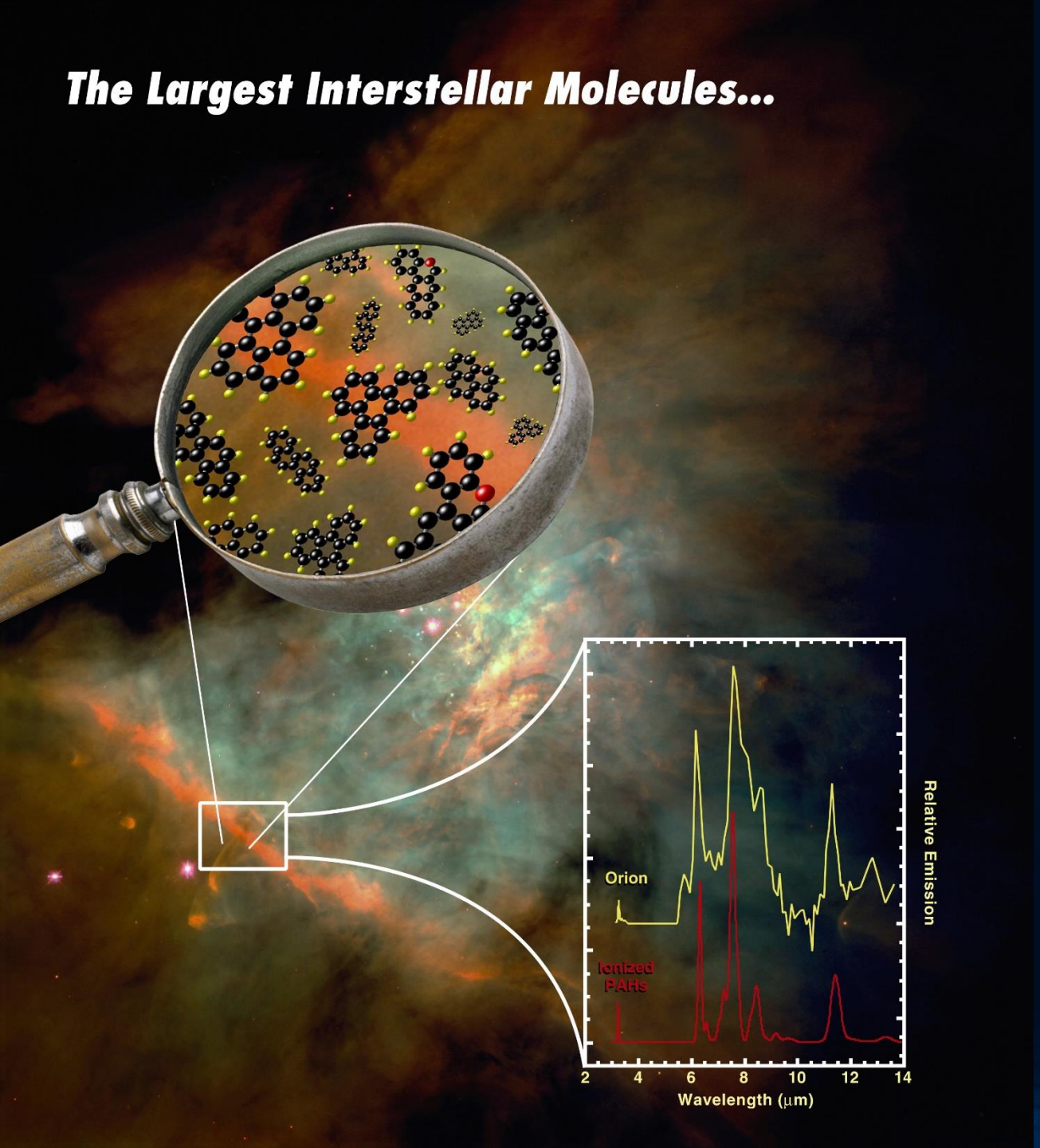
New Strategies of the Hybridized Carbyne-Based Nano-Matrix Spatially Controlled Growth During Ion-Assisted Pulse-Plasma Deposition

Alexander LUKIN
Oğuz Gülseren

lukin@wcrc.ru
gulseren@fen.bilkent.edu.tr

Western-Caucasus Research Center, Tuapse, Russian Federation
Department of Physics, Bilkent University, Ankara, Turkey
AIAA Solid Rockets Technical Committee (SRTC)

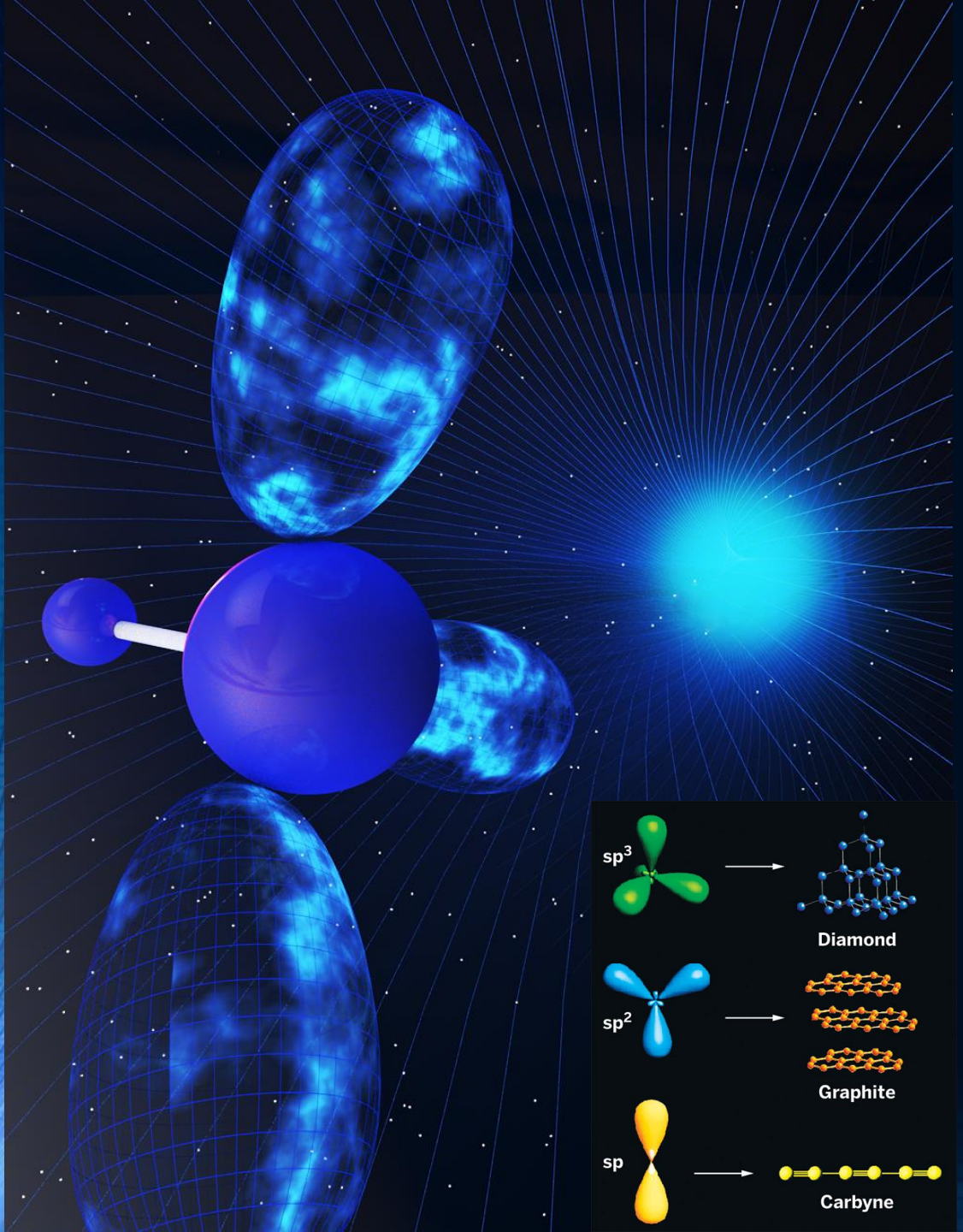
This research work is jointly supported and funded by the Scientific and Technological Research Council of Turkey (TÜBİTAK) and the Russian Foundation for Basic Research (RFBR) according to the research project № 20-58-46014



Understanding the Carbyne-Based Nanostructured Metamaterials

THE OBJECTIVE OF PRESENTATION

is to create an awareness of functionalized carbyne-based nanostructured metamaterials,
their molecular structure and spatial geometries,
new strategies for predictive designing their structure and properties and
how their use in future applications within the field of nanotechnology can benefit our society.



Understanding the Carbyne-Enriched Nanostructured Metamaterials: Carbyne is out-of-this-world interstellar material

Ideal one-dimensional form of carbon, a carbon allotrope - the linear-chain carbon, named as carbyne, attracted much interest due to advanced mechanical and electrical properties, including mechanical strength predicted to be an order of magnitude higher than that of diamond.

Like graphene, carbyne is just one atom thick, which gives it an extremely large surface area in relation to mass.

Back in the 1930s, astronomers detected carbynes as one of the first molecules in the interstellar space.

Later, astronomers have found the signs of the presence of cosmic carbyne crystals in interstellar dust clouds and in the material of some carbonaceous meteorites.

Nanostructured Metamaterial with Extraordinary Properties

Nano-Electronics

Nano-Membranes

Composites, Coatings, Thermal Protection

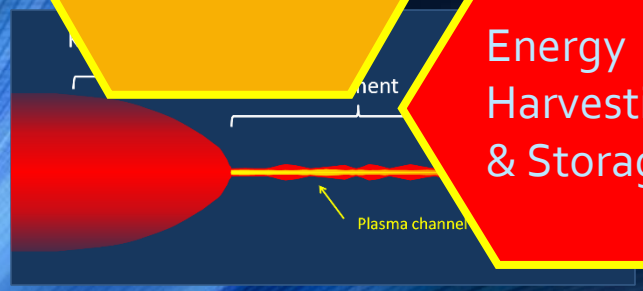
Sensors: Explosives Detection and Biosensors

Advanced Energetic Materials & Propellants

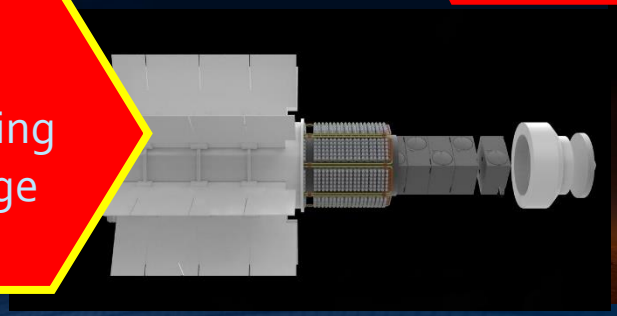
Key Application Areas for Carbyne-Enriched Nanostructured Metamaterials

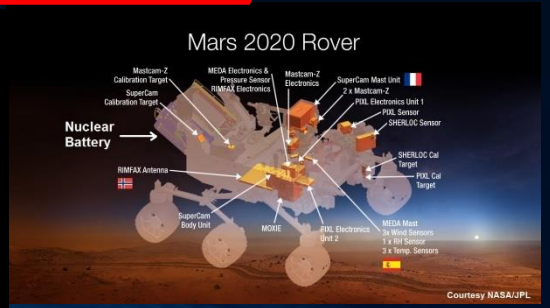
Multi-Mission Radioisotope Thermoelectric Generators

Biomedical Technologies



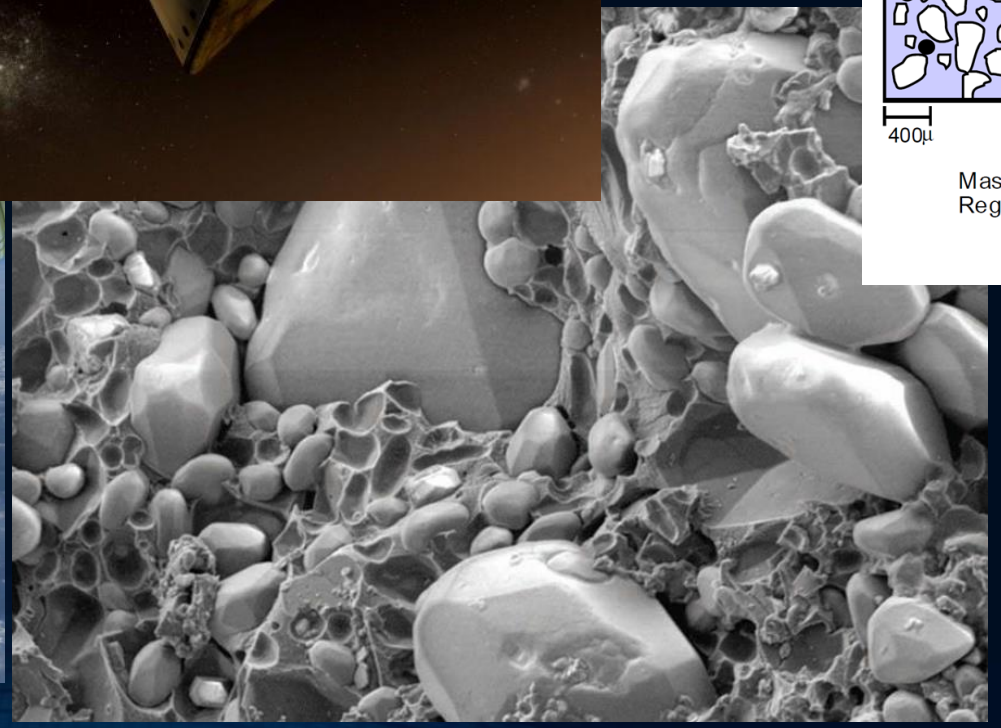
Energy Harvesting & Storage

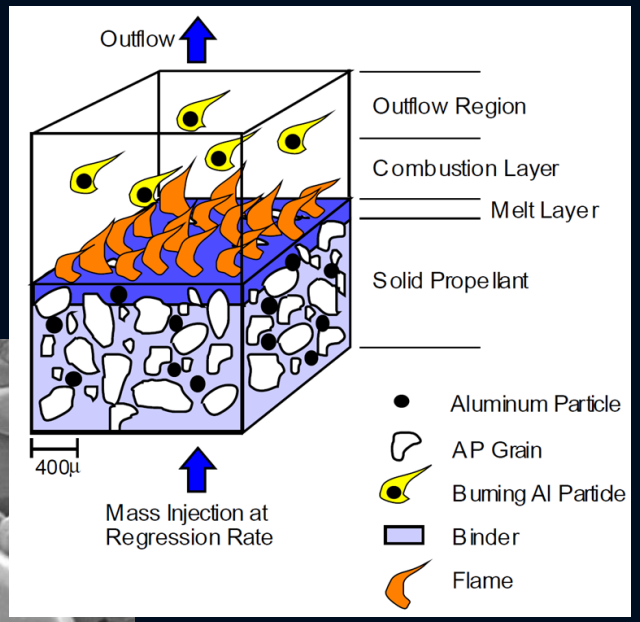




The Energetic Materials Performance Enhancement Through the Functionalized Carbyne-Enriched Nano-Sized Additives

Advanced Energetic Materials & Propellants



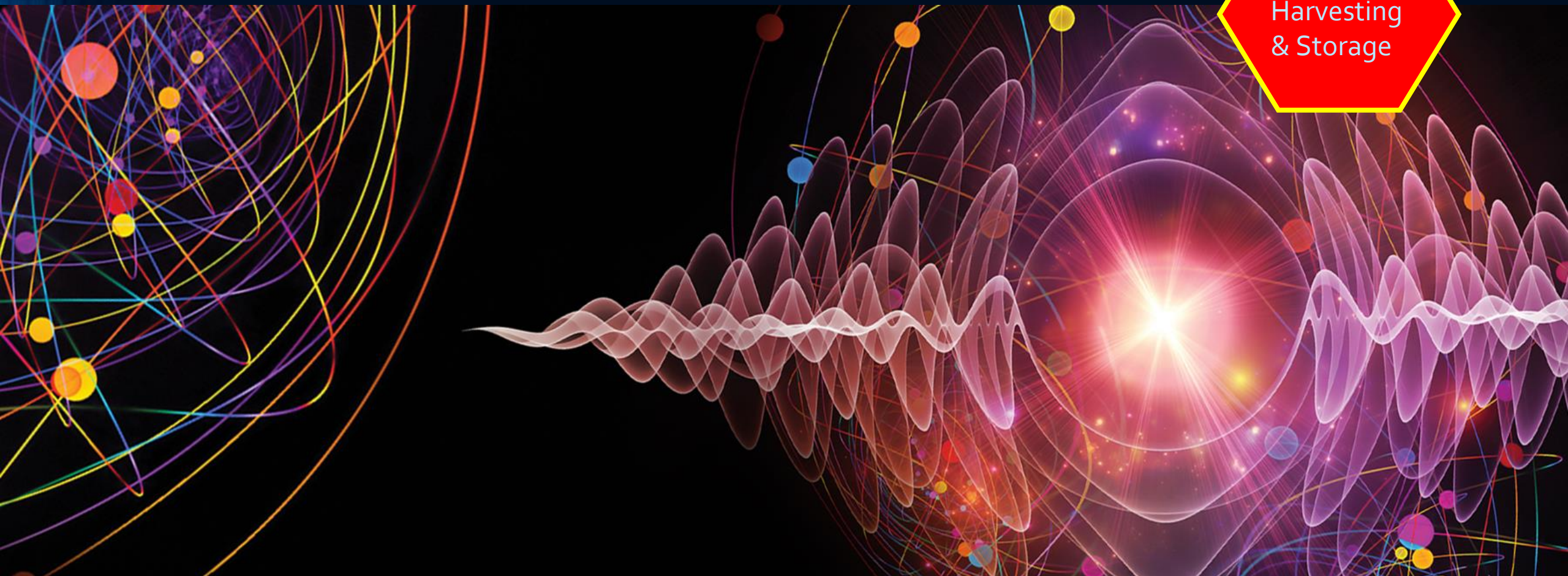


Nanostructured Carbon Metamaterials as Efficient Electrode Materials for Supercapacitor Applications

Carbyne-enriched carbon a novel high-performance electrode material for supercapacitor application.

Energy Storage Matrices like batteries and supercapacitors, where the surface area of the electrode determines energy density.

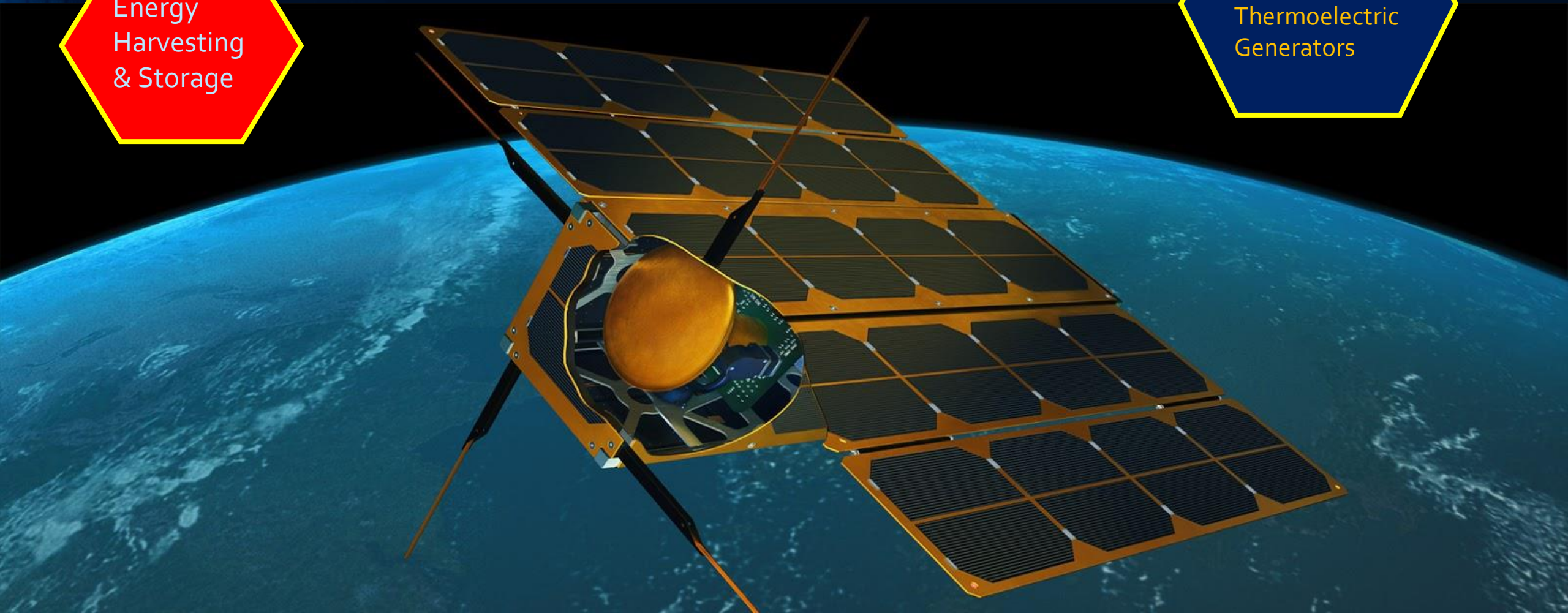
Energy Harvesting & Storage



Development the next generation of solar cells based on carbyne-enriched metamaterials

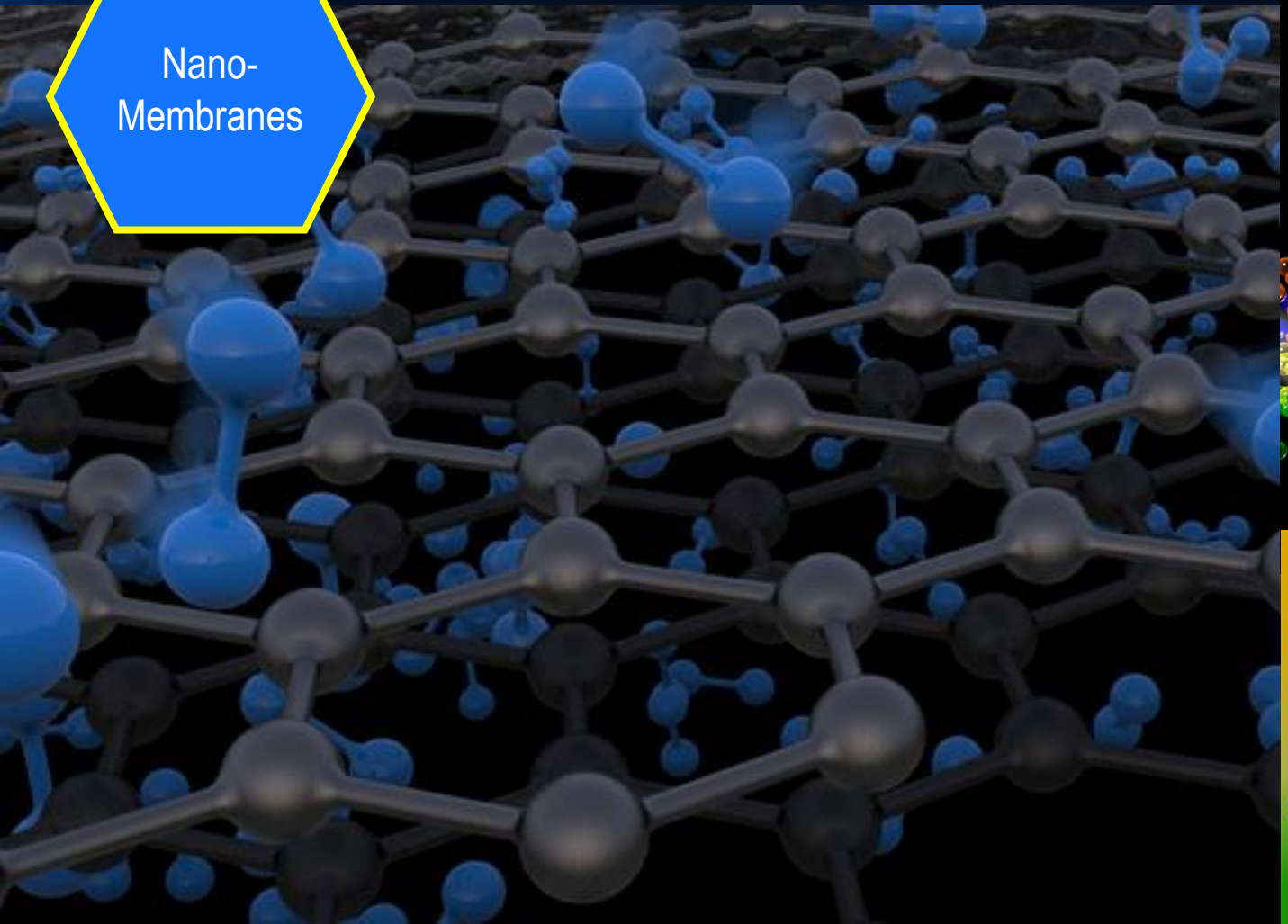
Energy Harvesting & Storage

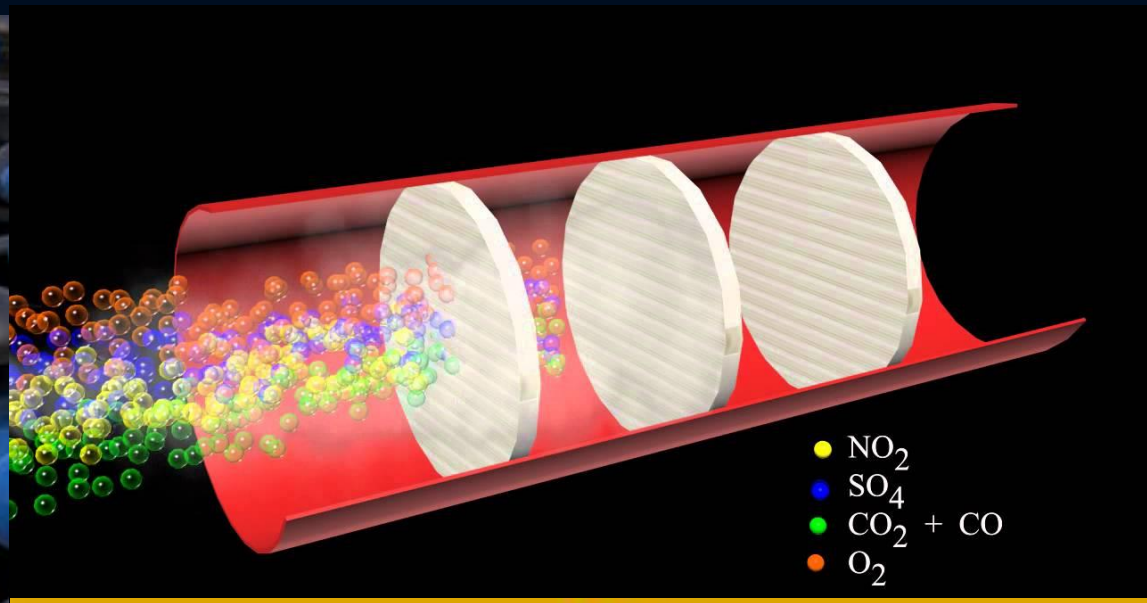
Multi-Mission Radioisotope Thermoelectric Generators

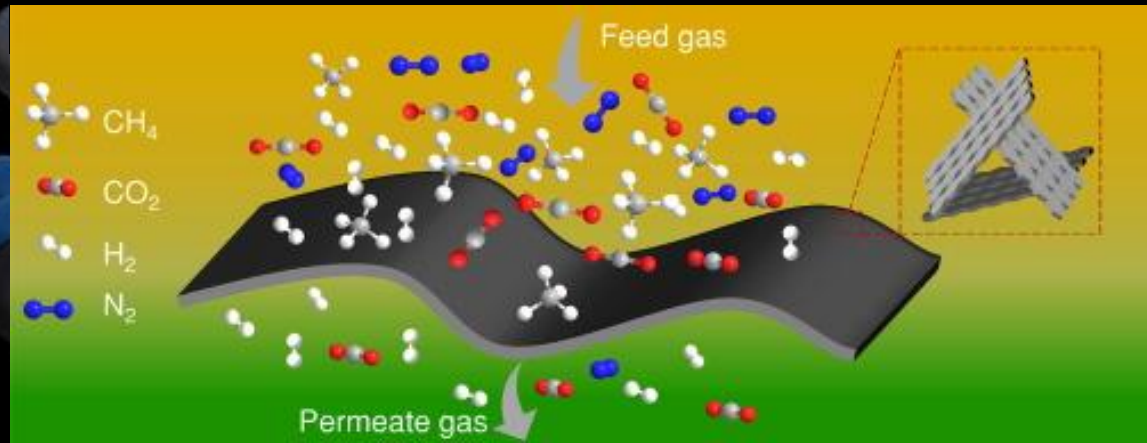


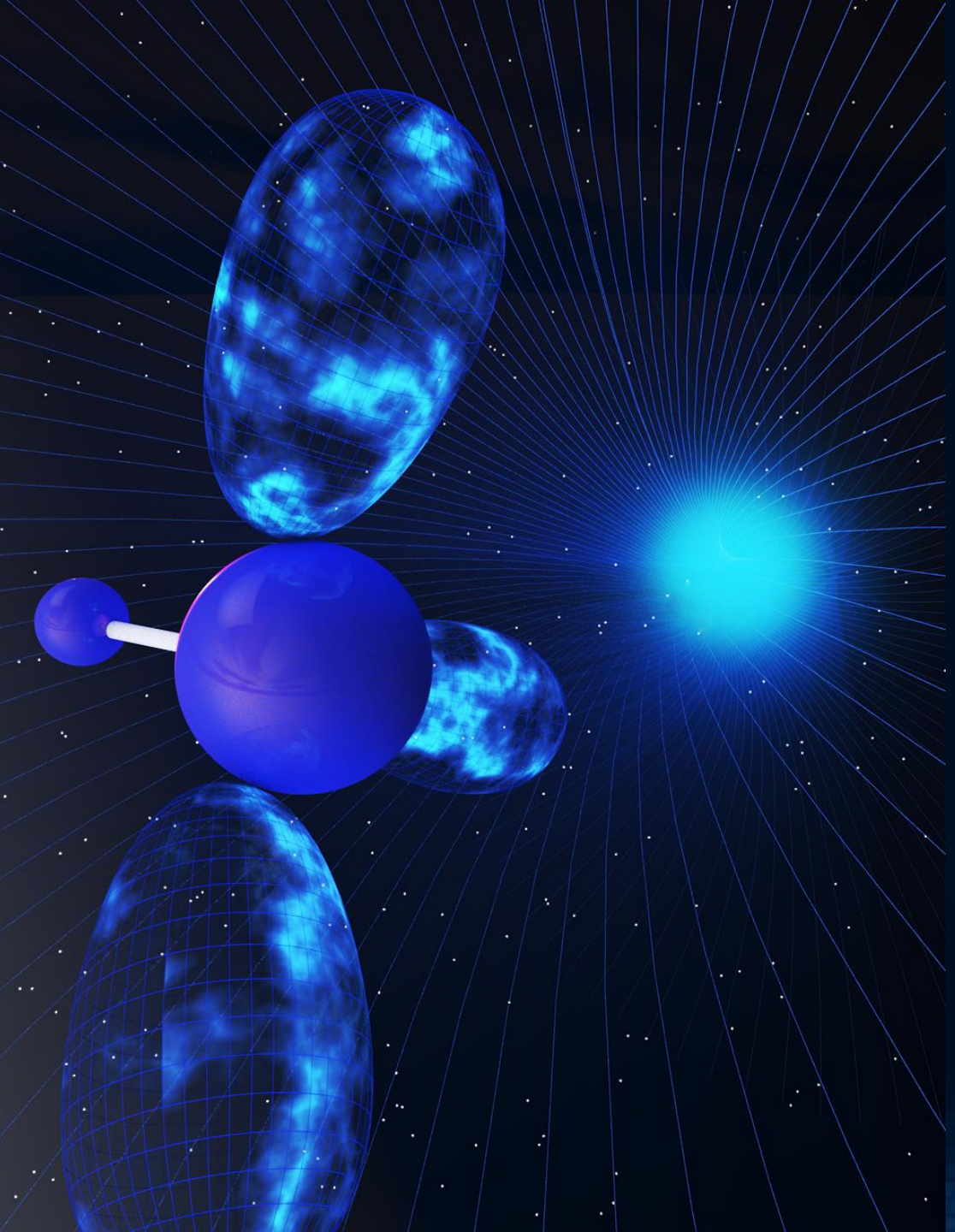
Development the next generation of carbyne-enriched active nano-membranes that allow continuous tuning of their functional parameters to target molecules by changing the parameters of the electric field in the pores.

Nano-Membranes







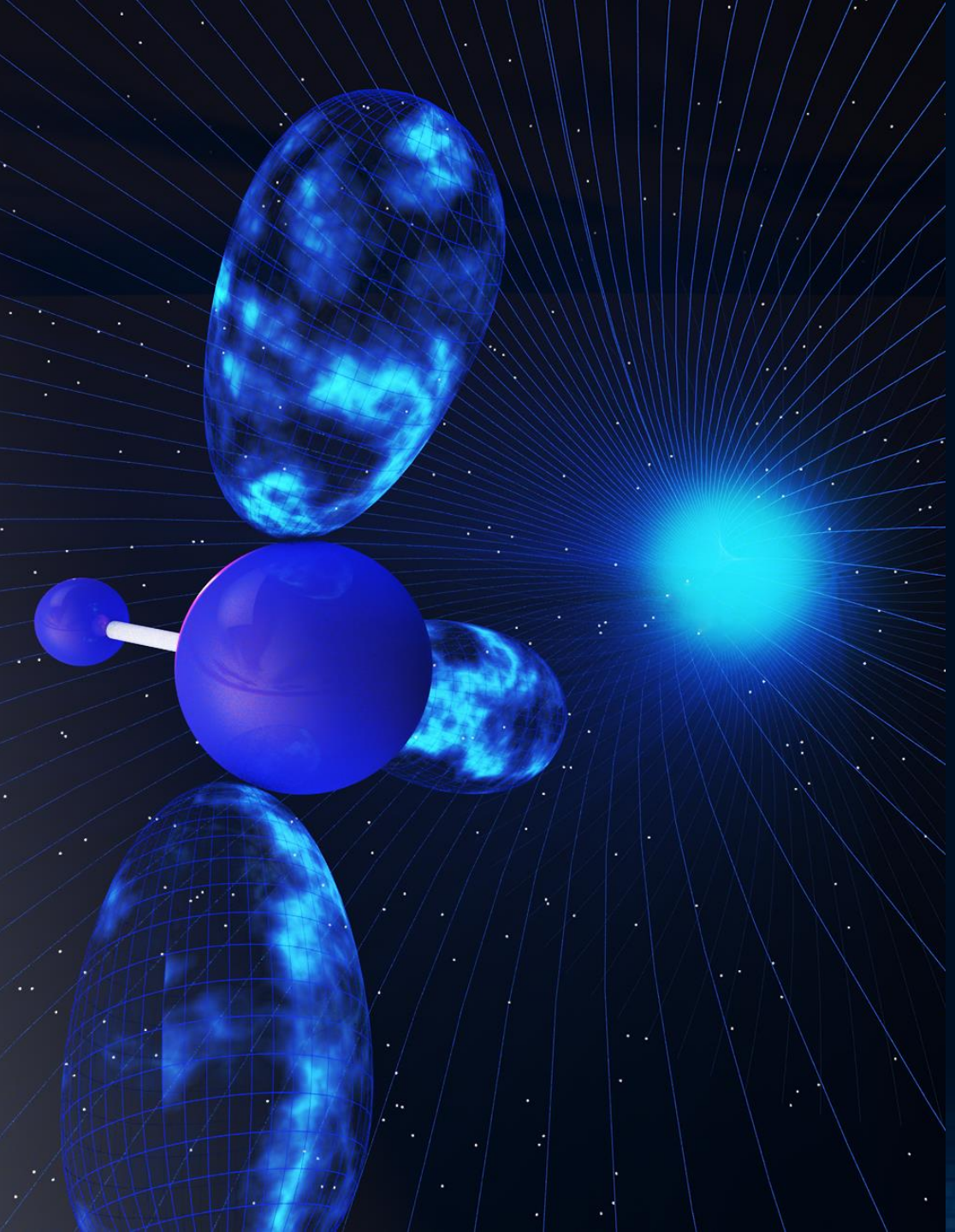


Carbyne is out-of-this-world interstellar material

The properties of the carbon-based nanostructured metamaterials essentially depend on their spatial structure.

Differently hybridized carbon atoms are capable to form diamond, graphite, linear-chain grids and many other specific allotropes.

Each carbon allotrope has notably different electronic and mechanical properties.



Carbyne is out-of-this-world interstellar material

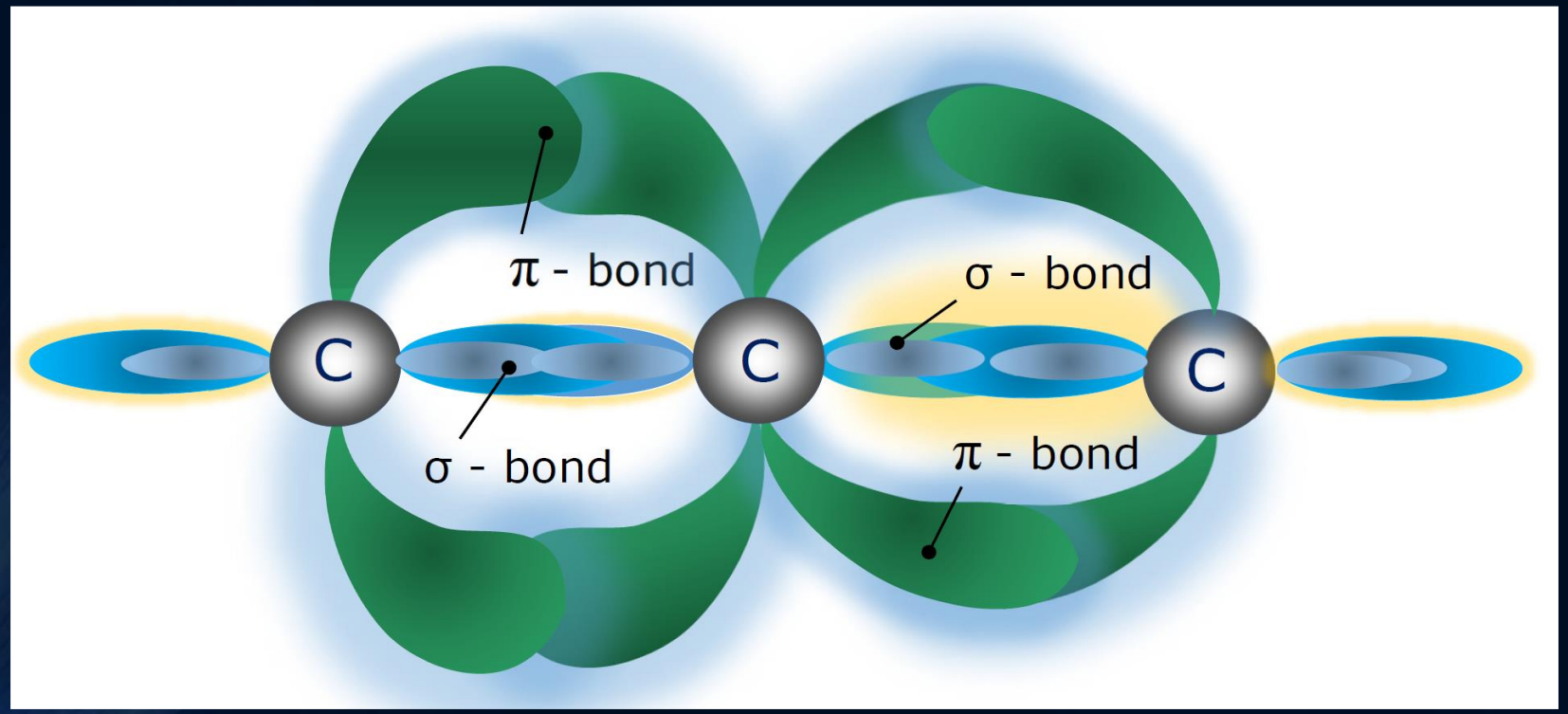
The existence of the cosmic carbyne can be used as a key to it formation mechanism and environments experienced by it and additionally confirms the presence of a factor of self-organization in the carbon chains growth.

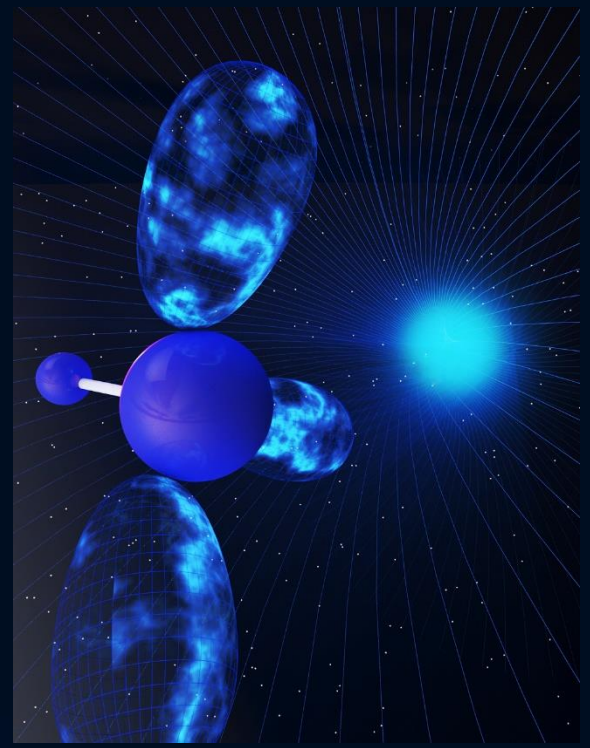
Linear chains are present in carbon vapors at temperatures above 5000 K.

The technology for growing this unique carbon nanostructured metamaterial is enough simple:
it self-organizes during condensation from carbon vapor in a vacuum at temperature above 3150 K.

The electronic structure of a linear-chain carbon molecule includes to kinds of bonds:

The sigma (σ) bond provides mechanical stability to the linear-chain carbon molecule, and the (π) bond, in addition to mechanical stability, provides the electrical properties of this nanostructure, since the π-electrons are delocalized and belong to the entire chain of atoms.





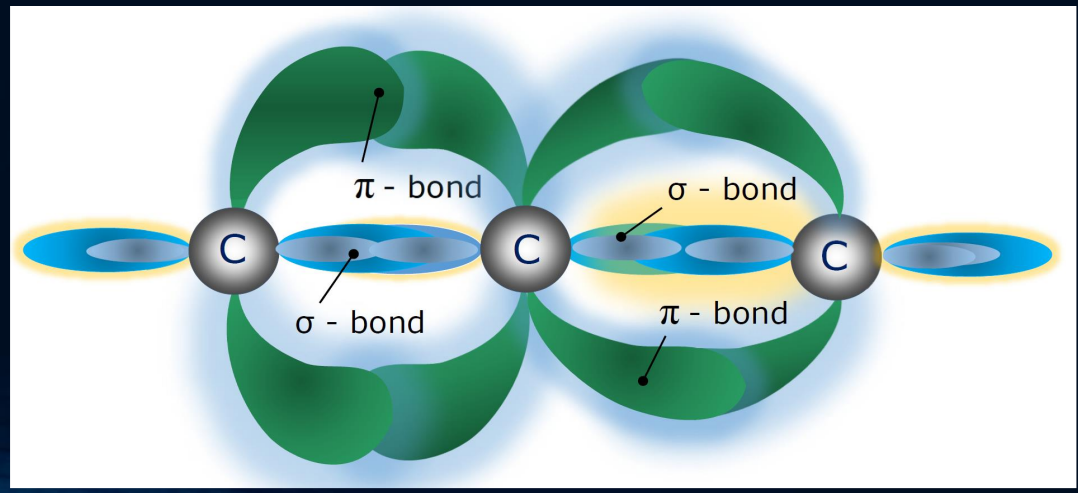
The electronic structure of a fragment of a linear-chain carbon molecule section

Carbyne – an unusual form of carbon

The growth of the macroscopic crystals of the carbyne is inhibited by the instability and high reactivity of this allotropic form of carbon.

Nanostructures stability depends from the linear carbon chains length.

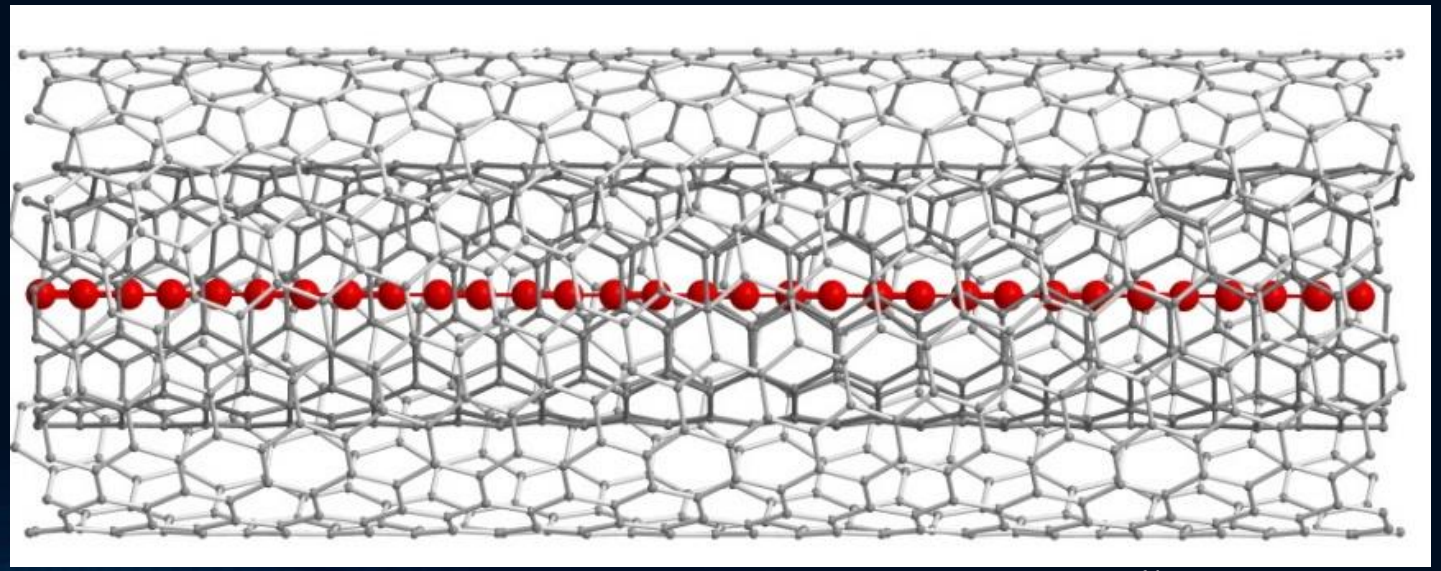
Most of current research efforts concentrated on searching possibilities for stabilization of the sp-hybridized carbon chains.



Stabilization of the Sp-Hybridized Carbon Chains

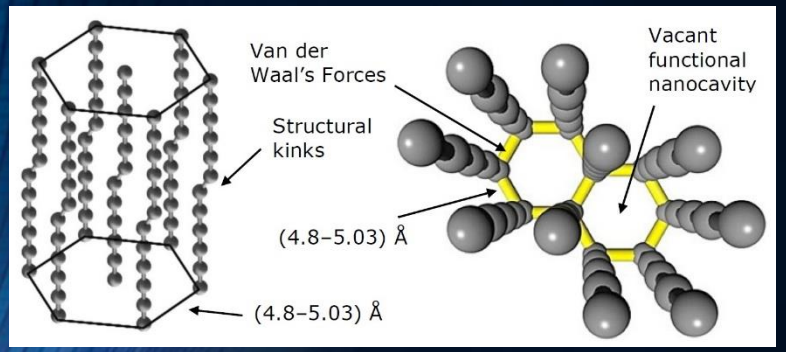
In 2016, a fundamentally new strategy was proposed and demonstrated to ensure the stability of the structure of the extremely long sp hybridized carbon chains containing more than 6000 carbon atoms
through growing within the long nano-matrices
formed by the double-walled carbon nanotubes.

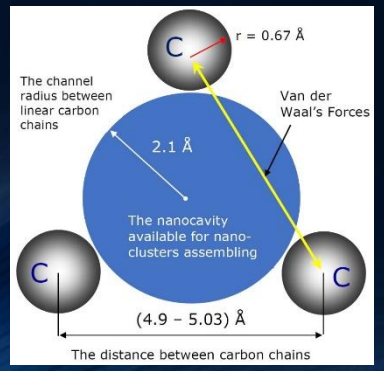
The thin double-walled carbon nanotubes surround the 1D carbyne molecule and protect it from inevitable disintegration.
This result showed the fundamental possibility of using the control of the nano-matrix structure for programming the stability of the carbon chains.



Shi, L., Rohringer, P., Suenaga, K. et al. Confined linear carbon chains as a route to bulk carbyne. Nature Mater 15, 634–639 (2016).

Stabilization of the Sp-Hybridized Carbon Chains





One of promising routes for growing of the carbyne-based nanostructured metamaterials is ion-assisted pulse-plasma deposition from the carbon plasma.

This technique was developed relatively recently and opens possibility for growing of stable carbyne-enriched nanostructures in the composition of multi-cavity nano-matrixes.

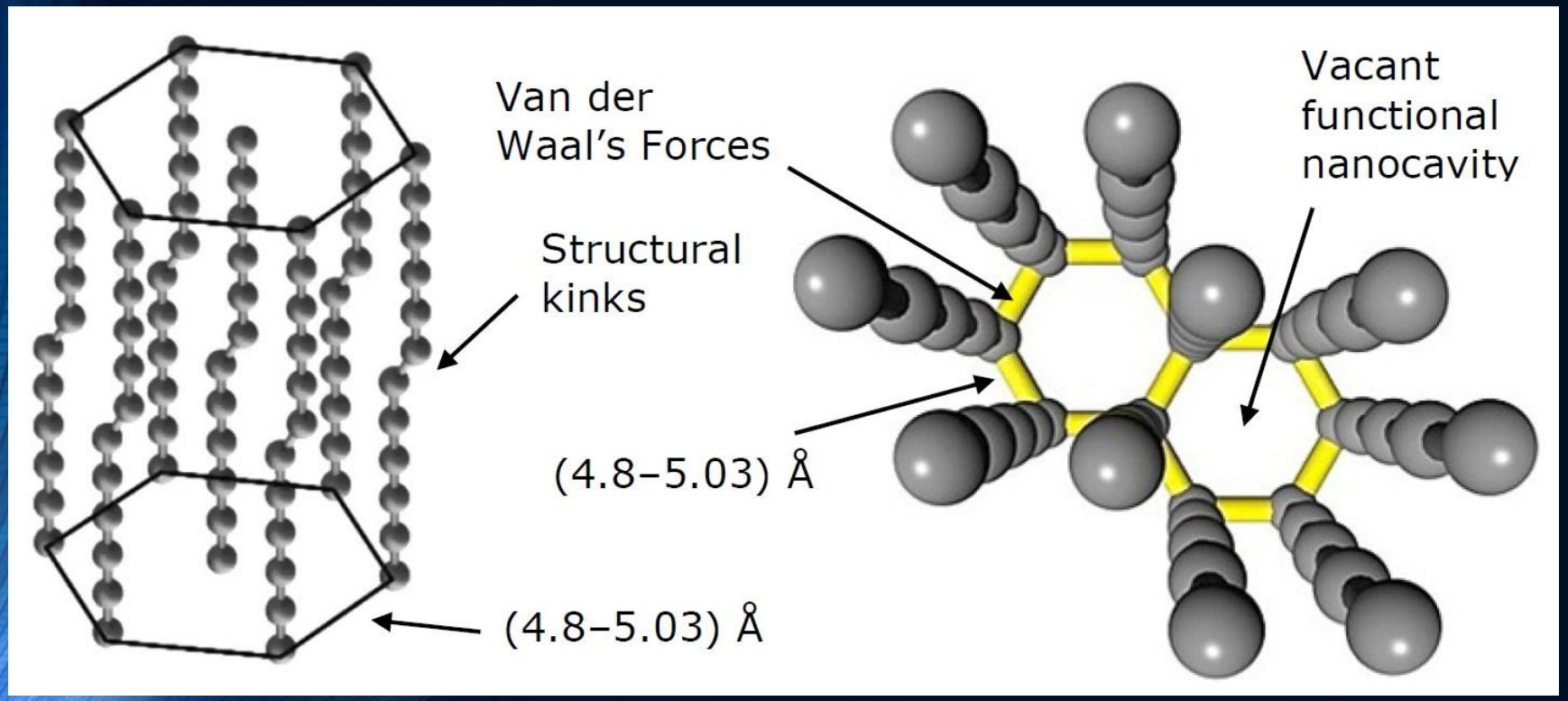
Such nano-sized carbon structures obtained the name as
two-dimensionally ordered linear-chain carbon,
which is a two-dimensionally packed hexagonal array of carbon chains
held by van der Waals forces at a distance of about 5 angstroms.

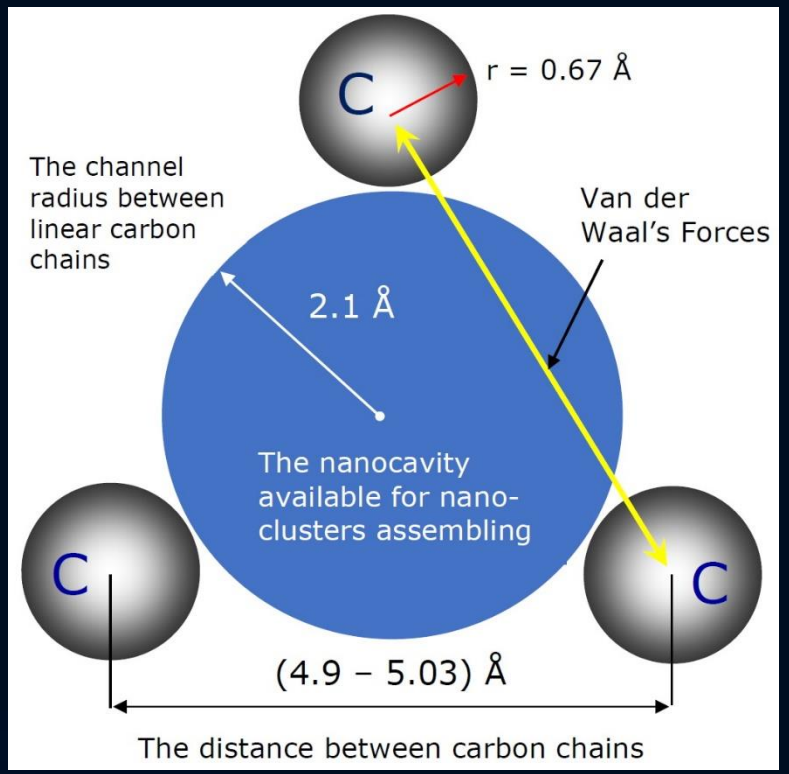
This technique also opens possibilities for further increase of the long carbon chains stability through assembling them by atomic clusters of different chemical elements, for instance, Silver, Gold, Titanium, etc.

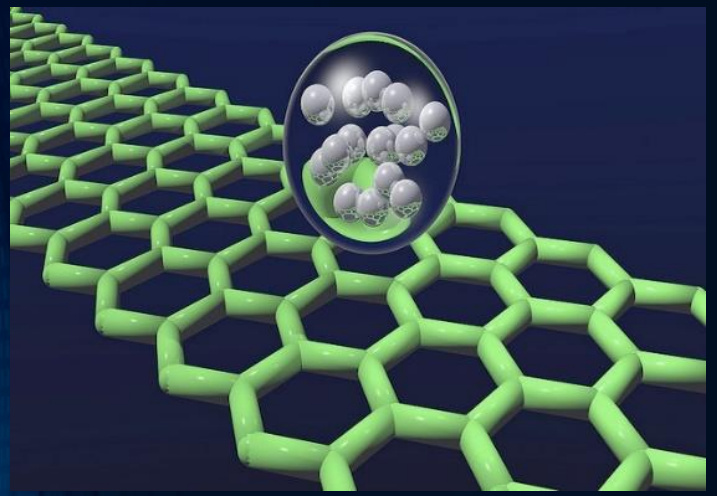
Due to outstanding deposition possibilities:
layer-by-layer deposition, possibility of metastable carbon phase synthesis,
low substrate heating, applicability for various substrate types,
this tool-kit continues studied Worldwide.

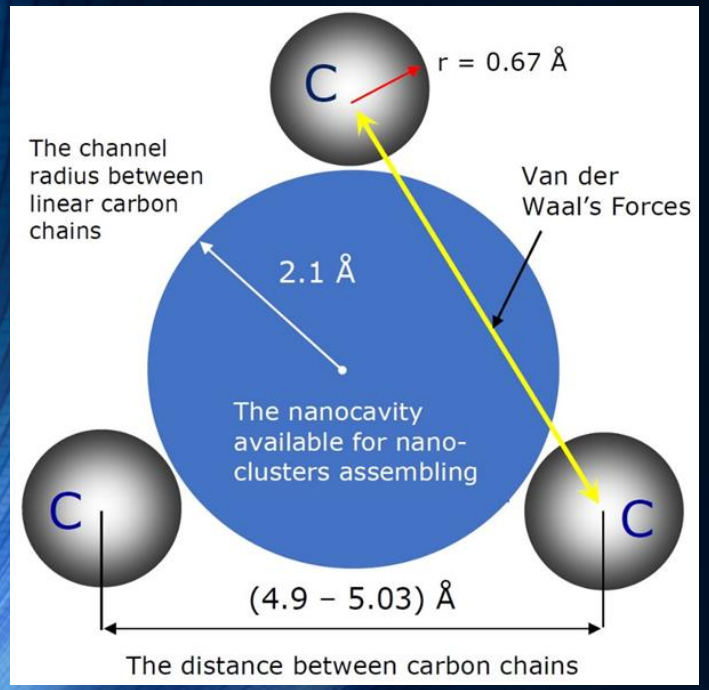
The model of spatial structure of the two-dimensionally ordered linear-chain carbon nano-matrix
The measured distance between the carbon chains is about (4.8–5.03) angstroms.

The vacant functional nanocavity available for the nano-clusters assembling.









Cluster-Assembling

Cluster-assembling of the nano-matrix can occurs both without chemical interaction (so called intercalation), and with rupture of the π bonds, which can leads to addition reaction.

For instance, assembling two-dimensionally ordered linear-chain carbon with calcium clusters, which suck up hydrogen molecules, creates a high-density, reversible hydrogen storage device.

The two-dimensionally ordered linear chain carbon nano-matrix could serve as an efficient basis for designing and the growth of the new carbon-based nanostructured metamaterials with unique electrophysical, optical, structural, topographic, biological and chemical properties.

Pulse-Plasma Experimental Set-Up

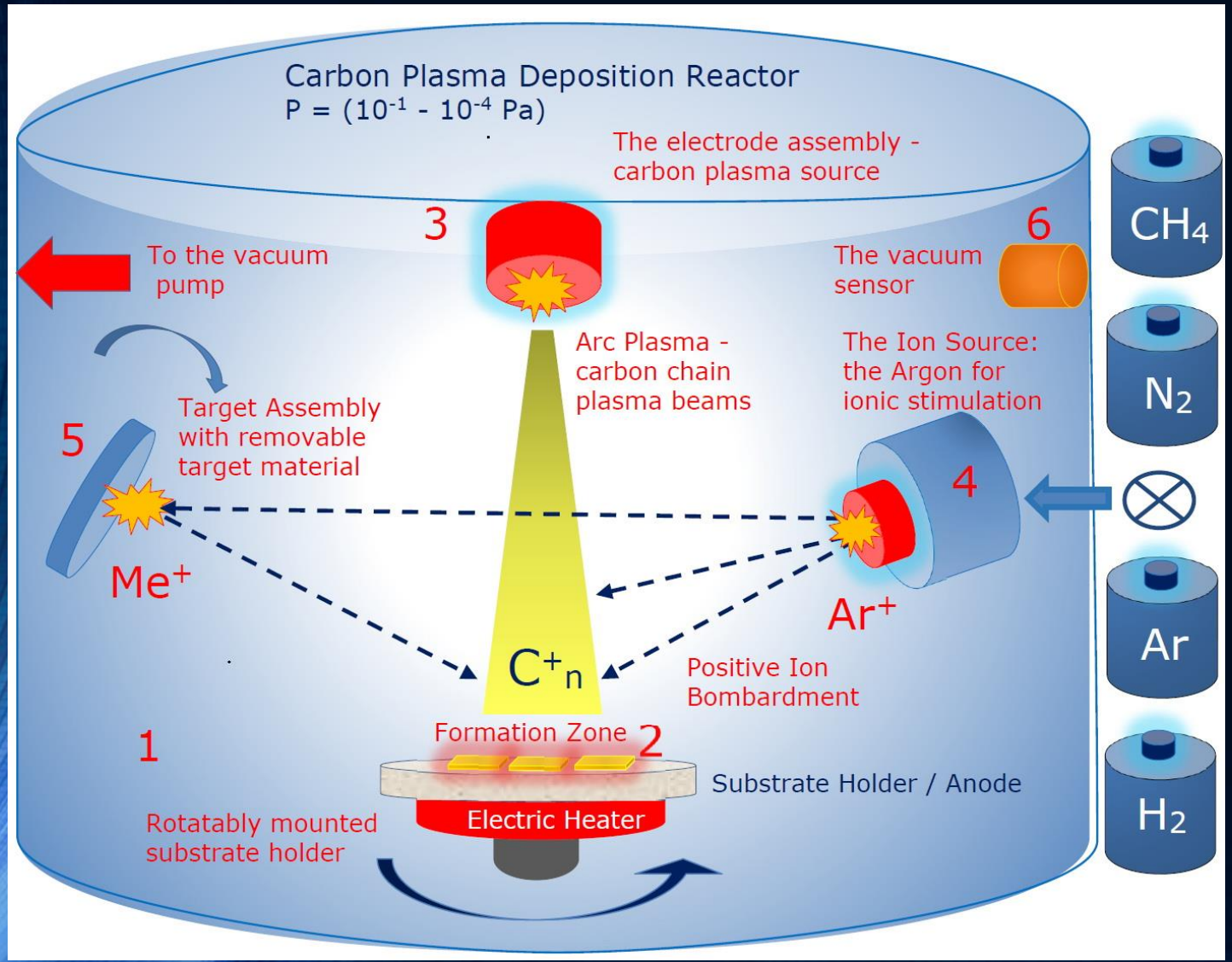
Cathodic Arc Plasma Deposition or Arc-PVD (PVD is Physical vapor deposition)

is a physical vapor deposition technique in which an electric arc is used to vaporize material from a cathode target.

The vaporized material then condenses on a substrate, forming a thin nano-martix.

The experimental set-up for ion-assisted pulse-plasma deposition of the two-dimensionally ordered linear-chain carbon nano-matrix with capability of cluster-assembling by various specific catalytic agents and chemical elements .

Pulse-Plasma Deposition Reactor for growing of the carbyne-based nanostructures



Schematic representation of the carbon pulse-plasma deposition reactor for growing of the carbyne-based nanostructures:

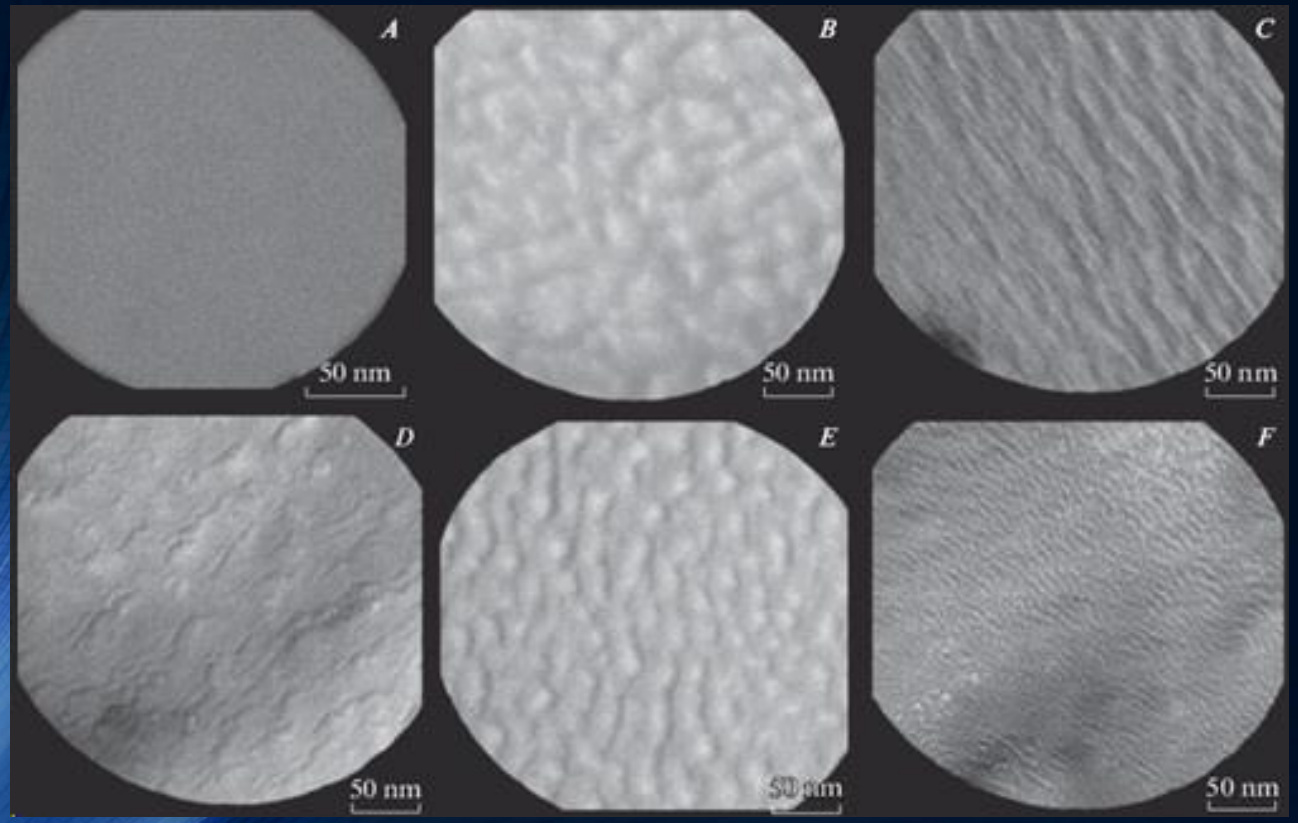
1 - vacuum chamber; 2 - substrate; 3 - pulse-plasma carbon generator (graphite cylindrical cathode of main discharge); 4 - the ion source for ionic stimulation; 5 - target assembly with removable target material; 6 - vacuum sensor.

The ion beam irradiation of the substrate surface forms bends in the attached carbon chains which stabilize the growing chain ensemble.

The experimental set-up for ion-assisted pulse-plasma deposition of the two-dimensionally ordered linear-chain carbon nano-matrix with capability of cluster-assembling by various specific catalytic agents and chemical elements .

The structure of the film deposited without ion assistance is homogeneous, while the structure of ion-assisted samples is heterogeneous.

The specific conductivity of ion-assisted films is 10^3–10^4 times larger than the conductivity of the films deposited without ion assistance.



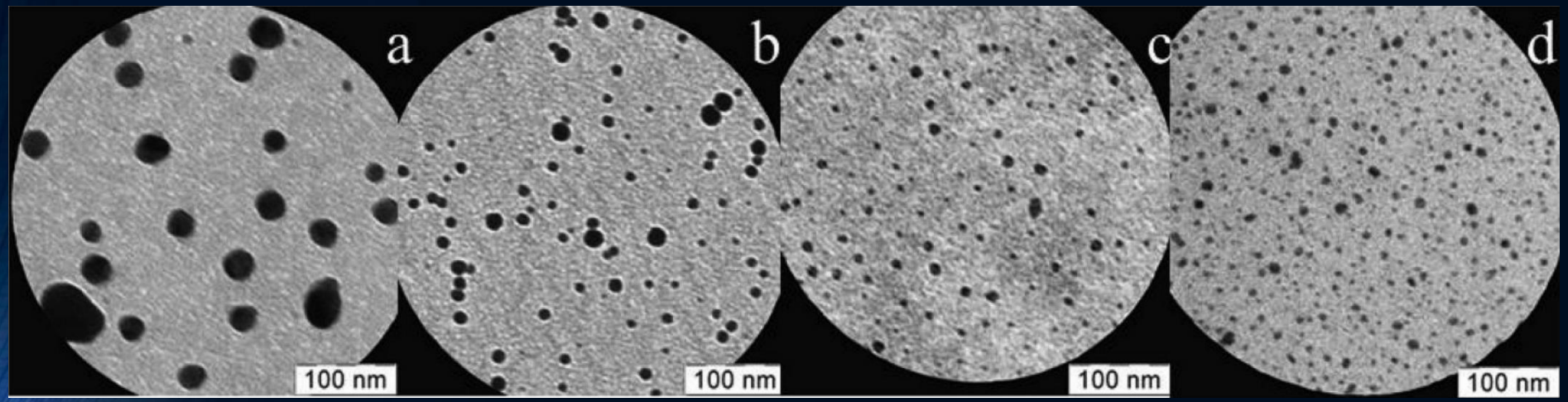
Transmission electron microscopy (TEM) patterns of samples obtained in different conditions: (A – 0 eV, B – 200 eV, C – 300 eV, D – 400 eV, E – 600 eV, F – 800 eV).

Streletskiy O.A., Zavidovskiy I.A., Nischak O.Y., Haidarov A.A., Size Control of Silver Nanoclusters During Ion-Assisted Pulse-Plasma Deposition of Carbon-Silver Composite Thin Films, Vacuum, 2020, vol 175, pp. 109286

Assembling of the caron nano-matrix by silver nanoclusters.

The transmission electron microscopy images of the samples, obtained at application of different ion assistance energies.

At increase of the energy flux into the deposition region occurs decrease of the average size of the active nucleation centers at simultaneous increase in their numbers.

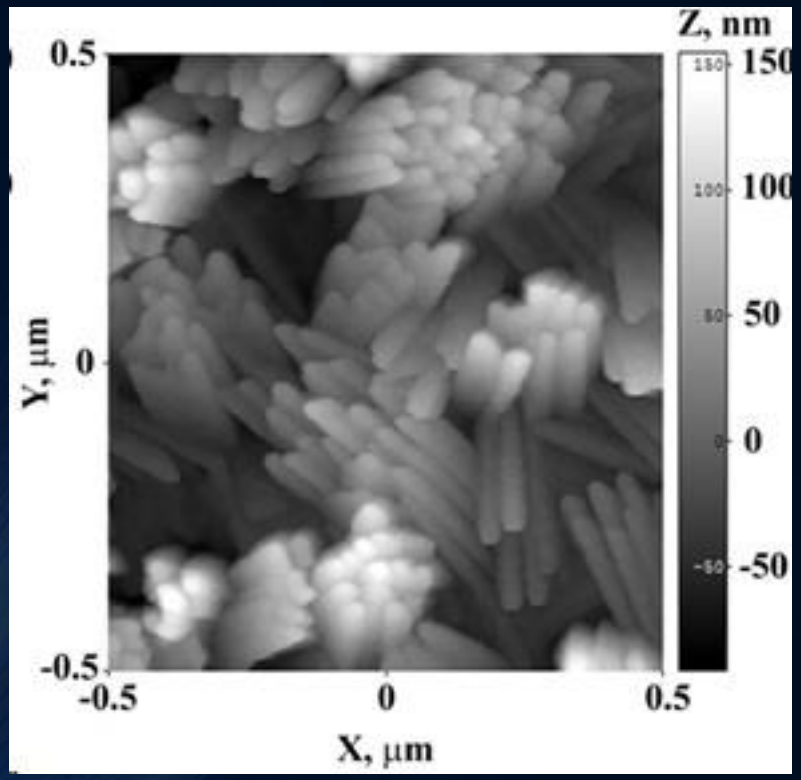


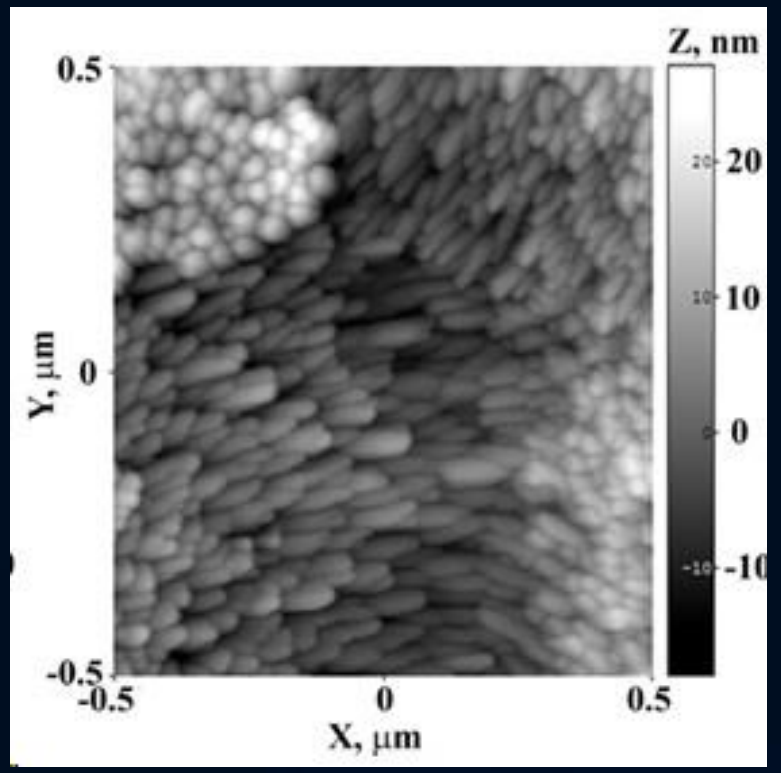
TEM images of the samples deposited at different ion assistance energies: (a) 0 eV, (b) 100 eV, (c) 200 eV, (d) 300 eV.

Streletskiy O.A., Zavidovskiy I.A., Nischak O.Y., Haidarov A.A., Size Control of Silver Nanoclusters During Ion-Assisted Pulse-Plasma Deposition of Carbon-Silver Composite Thin Films, Vacuum, 2020, vol 175, pp. 109286

Spatial pattern formation under external vibrations

As can be seen from the atomic force microscopy (AFM) images of 150 nm thick Tellurium nanostructures, the acoustic waves applied to the substrate results in morphological changes, demonstrated self-organizing of the nanostructures.



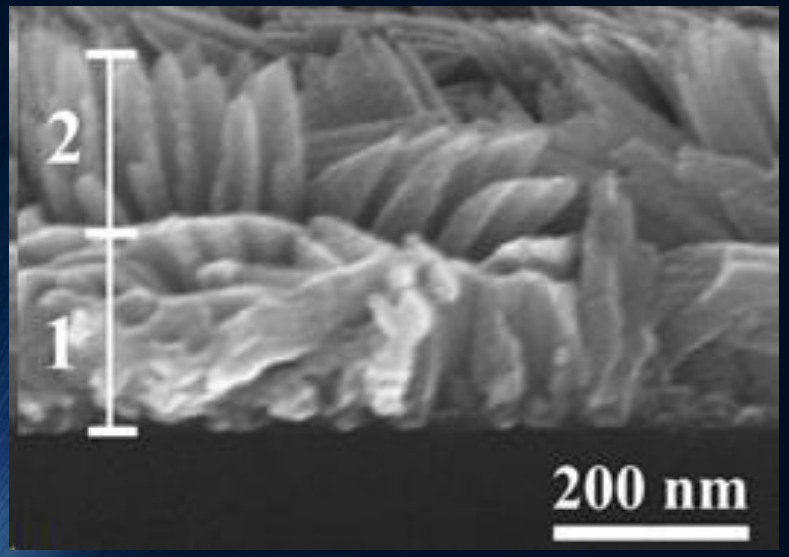


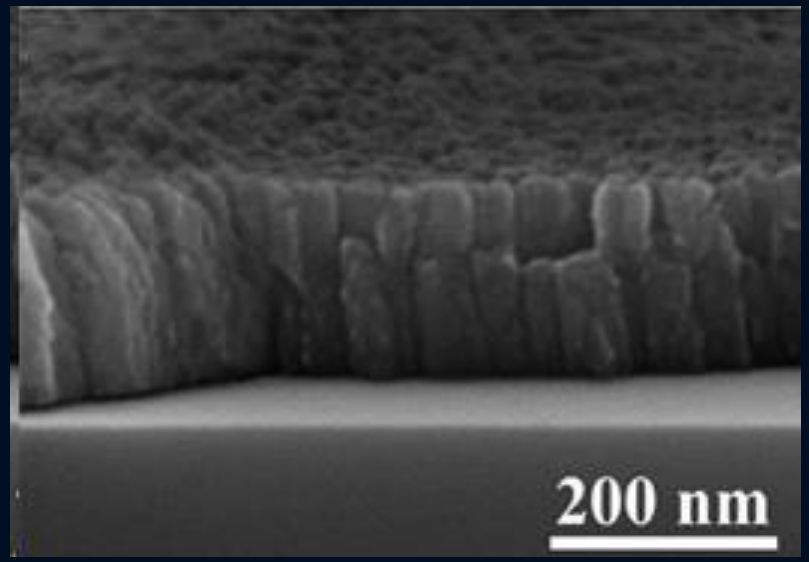
The atomic force microscopy (AFM) images of 150 nm thick Tellurium nanostructures, deposited at mechanical vibration frequencies of a) 50 Hz and b) 4 kHz.

T. Hristova-Vasileva, I. Bineva, A. Dinescu, D. Arsova a, D. Nesheva, "Cymatics" of selenium and tellurium films deposited in vacuum on vibrating substrates, Surface & Coatings Technology 307 (2016) 542–546

Spatial pattern formation under external vibrations

The acoustic waves applied on the substrate results in more significant morphological changes in the Tellurium nanostructures in comparison with Selenium nanostructures.
The Fig (a) corresponding to the mechanical vibrations frequency of 50 Hz demonstrates a graded and highly disoriented nanostructure.
The Fig. (b) corresponding to the mechanical vibrations frequency of 4 kHz is observed ordered columnar nanostructure.





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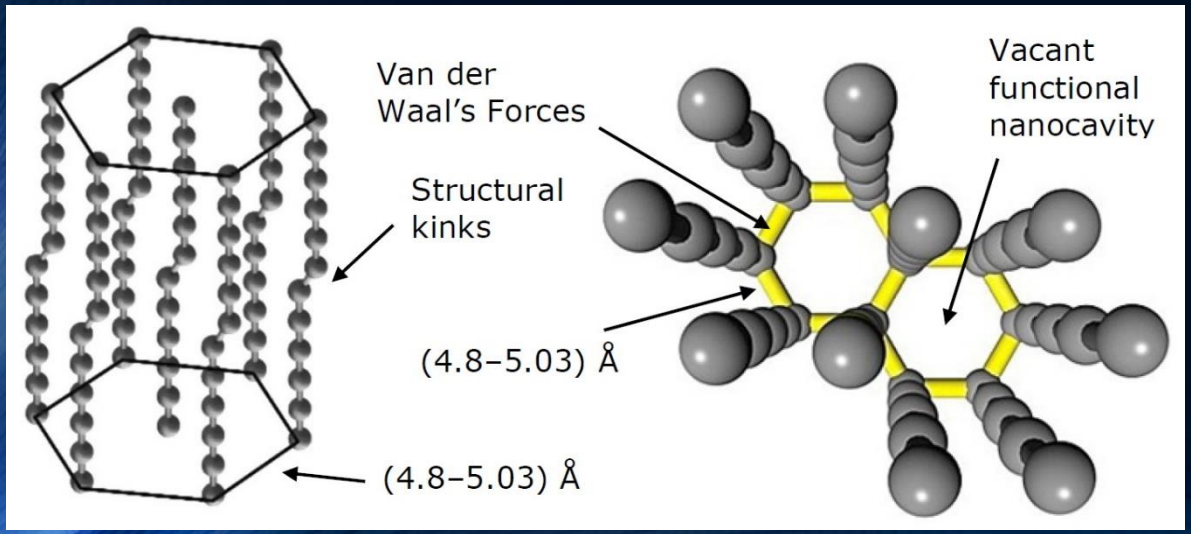
Cross-section scanning electron microscopy (SEM) microphotographs of the Tellurium nanostructures with magnification of 105 times. During deposition were applied the following frequencies: a) 50 Hz, (1 - dense part; 2 - highly porous part) and b) 4 kHz.

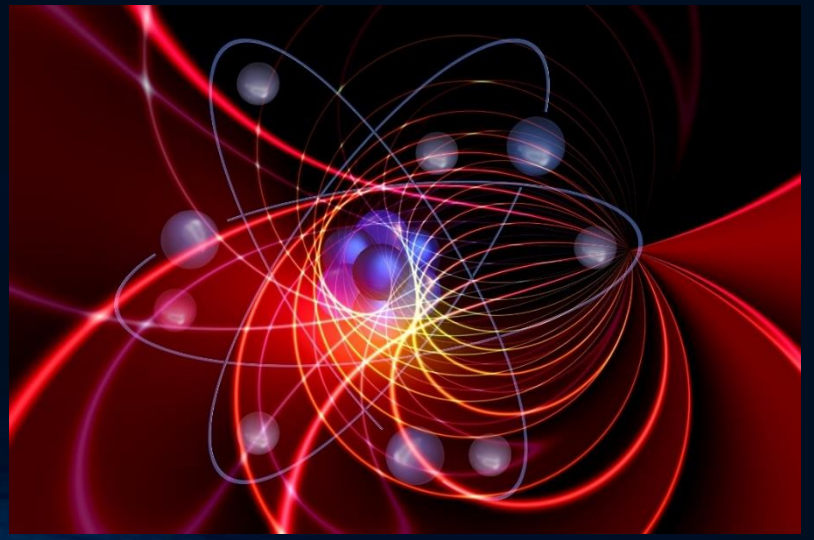
Vibration-Assisted Growing of the Carbyne-Enriched Nano-Matrixes

With taking into account the high sensitivity of the structure of a two-dimensionally ordered linear-chain carbon to ultrasonic vibrations, we propose a Concept of vibration-assisted excitation of self-organizing and pattern formation during growing of the carbyne-enriched nano-matrixes.

We propose to use the universal Cymatics phenomena to vibration-assisted predictive growth of the carbyne-enriched nano-matrix.

An acoustic hologram generated in the nanostructure growth zone is capable of controlling the growth process, cluster-assembling and formation of chemical bonds.



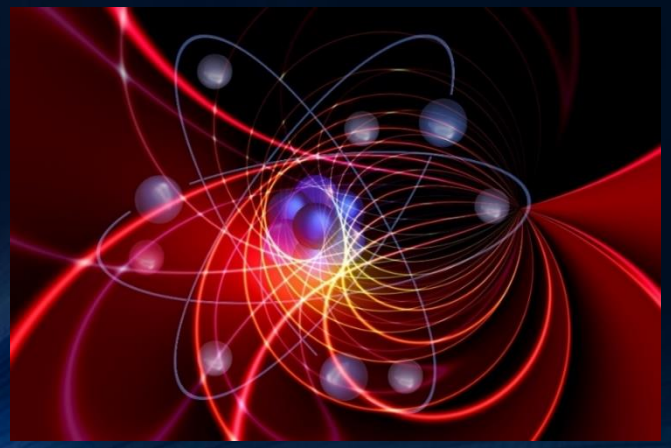


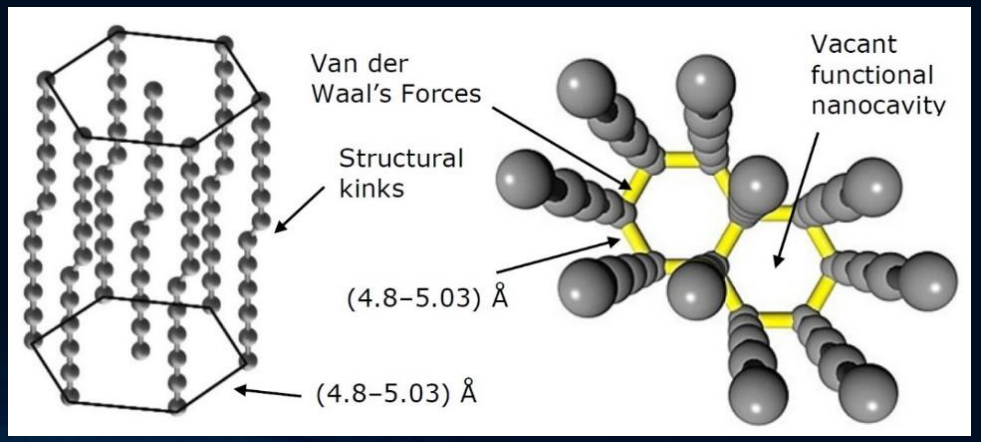
PLASMA-DRIVEN STRUCTURAL SELF-ORGANIZATION AND SURFACE PATTERN EXCITATION

Patterns excitation phenomena in the plasma deposition region is programmed by interaction of several competing mechanisms, in particular, through the thermo-electric convection excitation, by the state of stress in the deposited nano-matrix and by self-synchronization of the self-excited oscillatory cells in the deposition region.

Structural self-organization and pattern formation are the universal and key phenomena observed during growth and cluster-assembling of the carbyne-based nano-matrix at the ion-assisted pulse-plasma deposition.

Self-organization phenomena are observed also during the cluster-assembling of the nano-cavities by atoms of various chemical elements due to formation of new chemical, interatomic and intermolecular bonds.



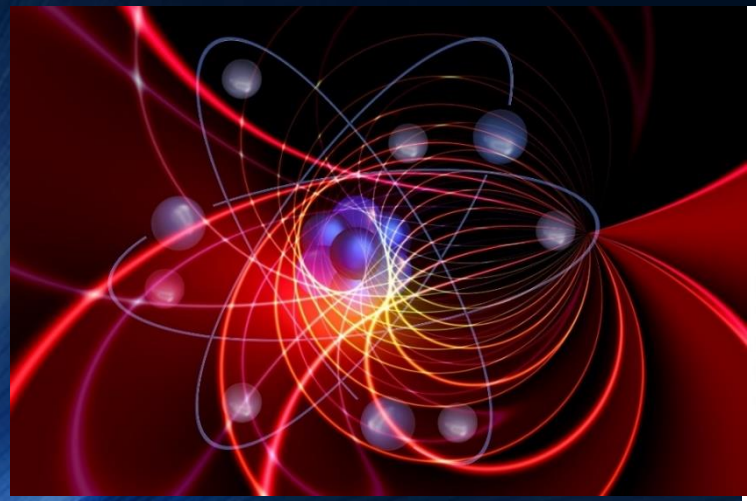


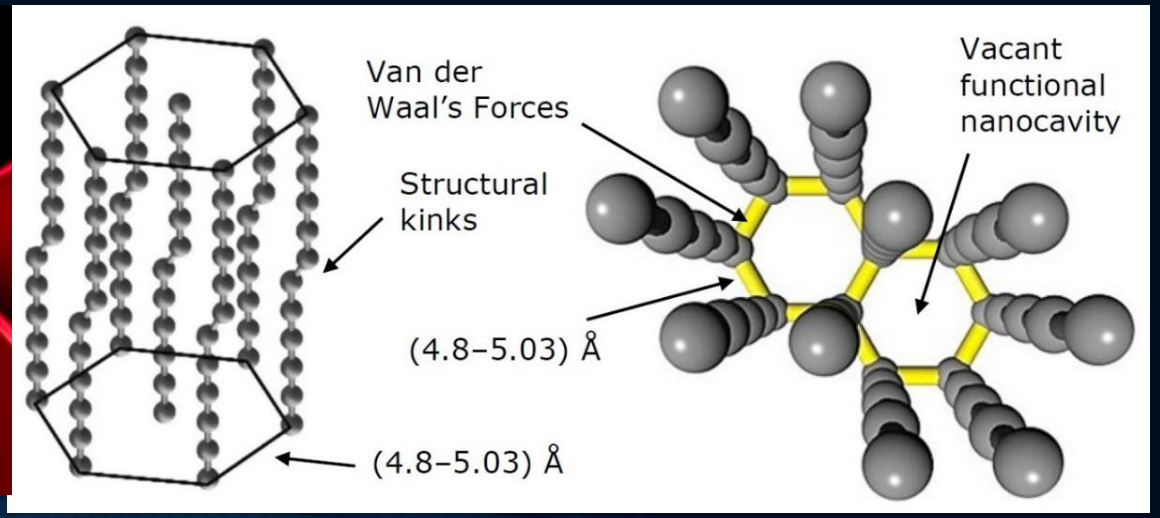
Vibration-Assisted Growing of the Carbyne-Enriched Nano-Matrixes

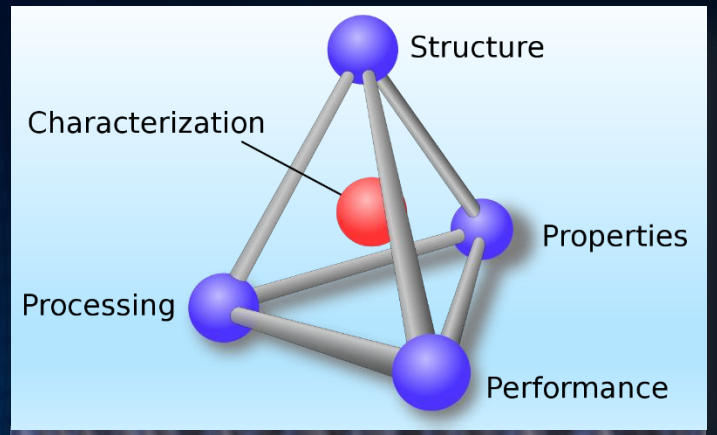
Certain frequencies of acoustic vibrations are capable of forming various geometric shapes.
This universal law can be used to program the structure of the grown nano-matrix.

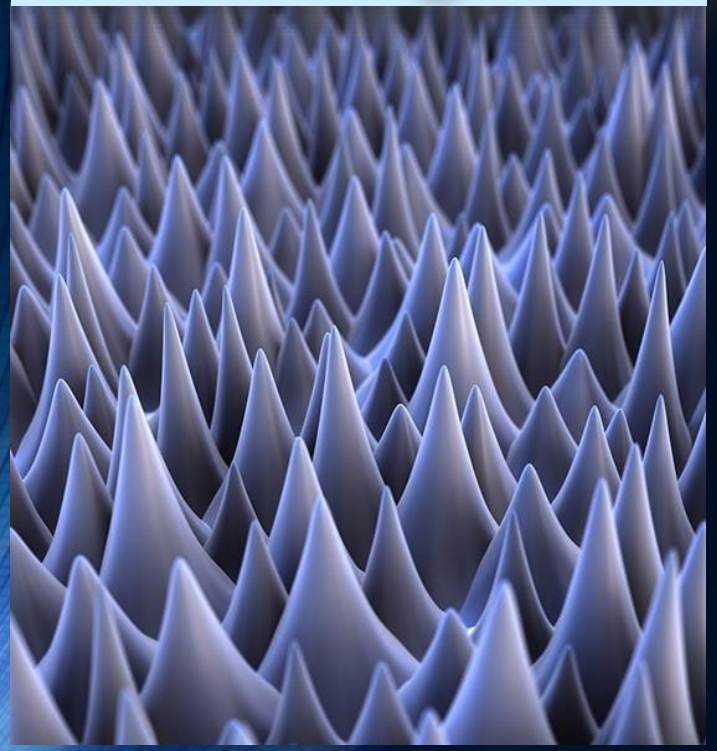
Since the nano-matrix is an acoustically sensitive material, we propose the technology for the patterning and control of the nanostructure growth onto acoustically excited piezoelectric substrates.

Assisting the plasma deposition of the nano-matrixes with acoustic waves (AWs) leads to patterning phenomena characterized by substantial lateral changes in nanostructure, thickness and properties. In addition, changes in crystal structure are also induced.









CONCLUSIONS

Structural self-organization and pattern formation are the universal and key phenomena observed during growth and cluster-assembling of the carbyne-based nano-matrix at the ion-assisted pulse-plasma deposition.

Manipulating by the self-organized patterns excitation we can provide controllable growth and programming of the properties of the functionalized carbyne-based nano-structures.

The two-dimensionally ordered linear chain carbon nano-matrix could serve as an efficient basis for designing and the growth of the new carbon-based nanostructured metamaterials with unique electrophysical, optical, structural, topographic, biological and chemical properties.

This research work is jointly supported and funded by the Scientific and Technological Research Council of Turkey (TÜBİTAK) and the Russian Foundation for Basic Research (RFBR) according to the research project № 20-58-46014

Thank you very much for your kind attention!