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Plasma design of 2D nanostructures and beyond graphene

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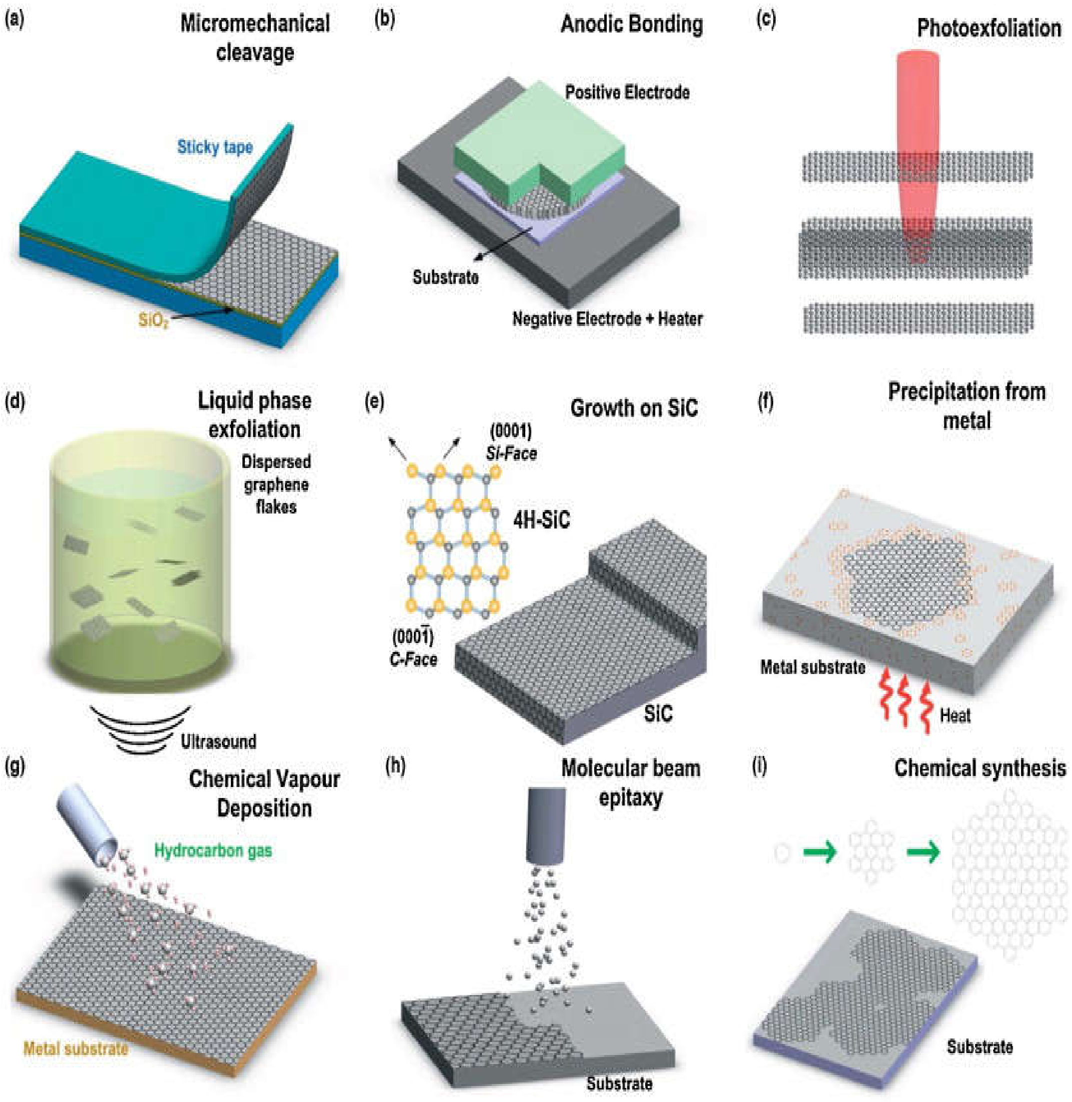
European Commission
HORIZON 2020
GRAPHENE PEGASUS

1. Introduction SofA and the 2D nanostructure case of graphene
2. Large-scale simulations
3. Experiments bottom-up
4. Experiments top-down
5. How to progress beyond graphene and the case of N-doping

Why Plasma-processing Techniques..?



Plasma assisted methods

- ❖ *Large scale growth with selected properties*
- ❖ *Control in ordering/patterning*
- ❖ *Rapid production and fast processing*
- ❖ *Easier and safer*

1. Y. L. Zhong, Z. Tian, G. P. Simon, and D. Li, Scalable production of graphene via wet chemistry: Progress and challenges, (2015).

2. O. Gökhan Eğilmez, Gürsel A. Süer,Özgüner, *Des. Control Appl. Mechatron. Syst. Eng.* 135 (2012).doi:10.5772/67458

TOP-DOWN approach

Syntheses

Low-pressure plasmas

Atmospheric-pressure plasmas

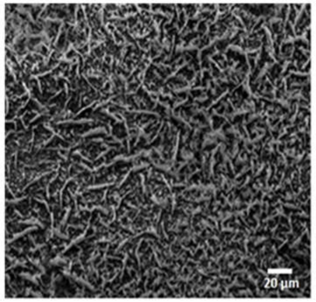
Different gas mixtures

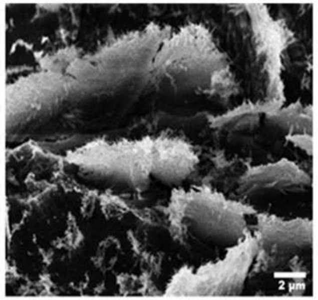
$Ar/H_2/CH_2$ $/C_2F_2$ ...

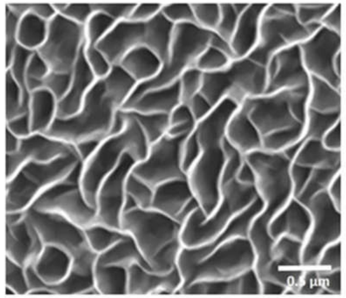
Post-processing

$Ar/N_2/NH_3$ ...

2D vertical graphene/N-graphenes







BOTTOM-UP approach

Use of gels (carbon precursors) + low pressure Ar/H_2 plasma

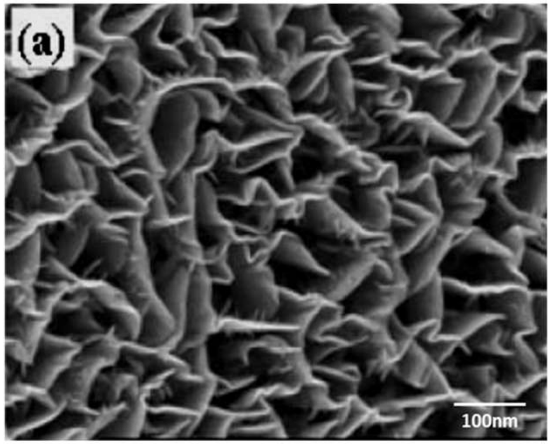
2D vertical graphenes → **N-graphenes**

Part 1 - INTRO TO SofA

Plasma-Assisted Synthesis Methods

Bottom-up approch

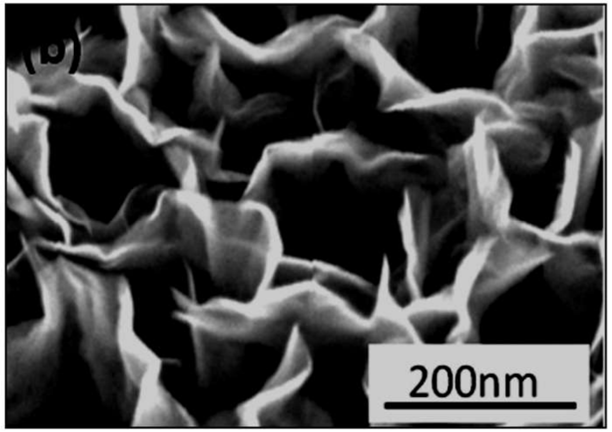
- Hydrocarbon/ Fluorocarbon gas sources
- Plasma interaction, deposition-nucleation and growth
- Plasma Enhanced Chemical Vapor Deposition (PECVD)



Wu, Y.; Yang, B.; Zong, B.; Sun, H.; Shen, Z.; Feng, Y. J. Mater. Chem. ***2004****, 14*

Top-down approach

- Solid/ Liquid carbon precursor
- Plasma treatment on the precursor and growth
- Plasma treatment on honey



Seo, D. H.; Rider, A. E.; Kumar, S.; Randeniya, L. K.; Ostrikov, K. Carbon N. Y. ***2013****, 60, 221–228*

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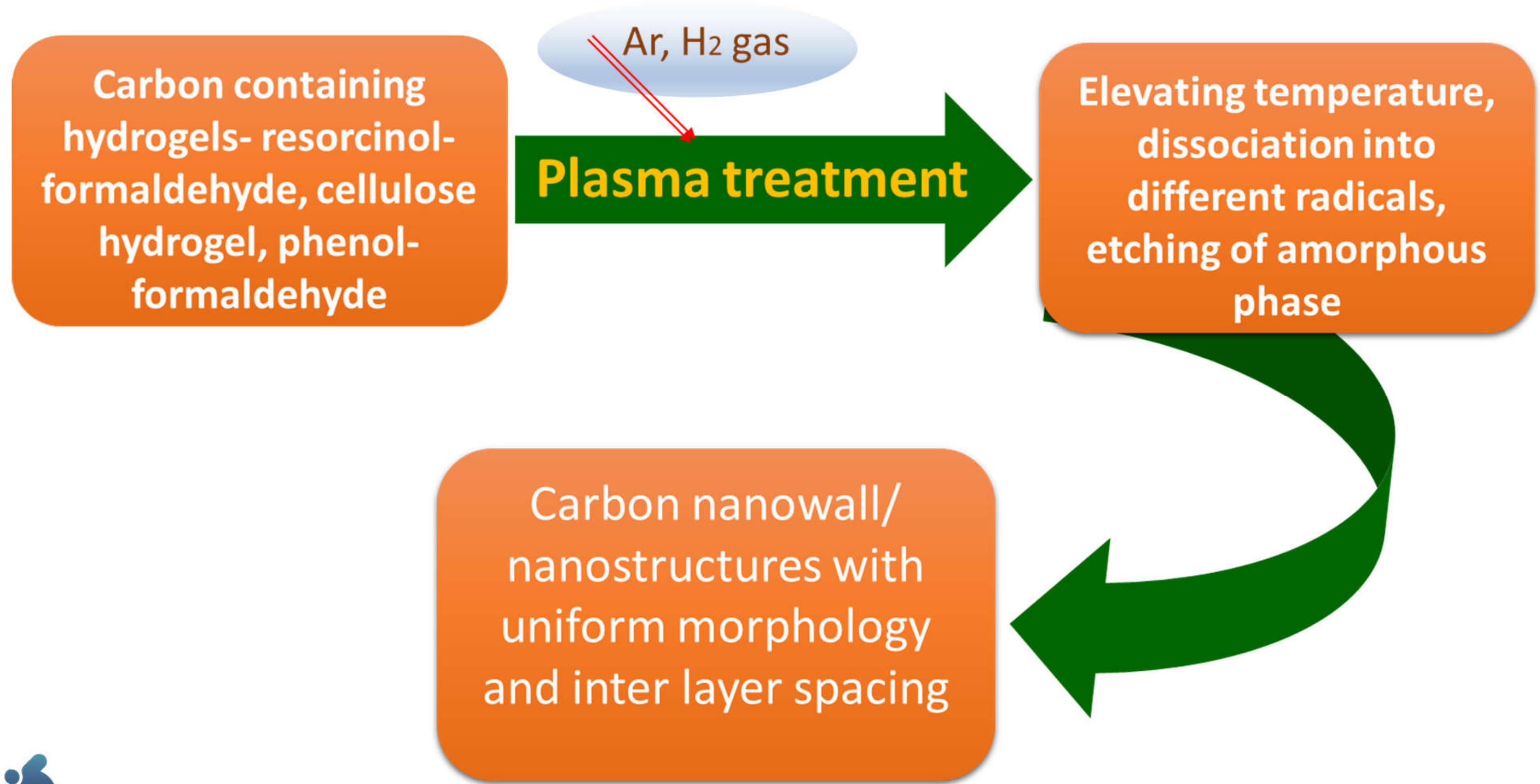
Plasma Treatment On Solid/Liquid Carbon Sources (and related environmental issues)



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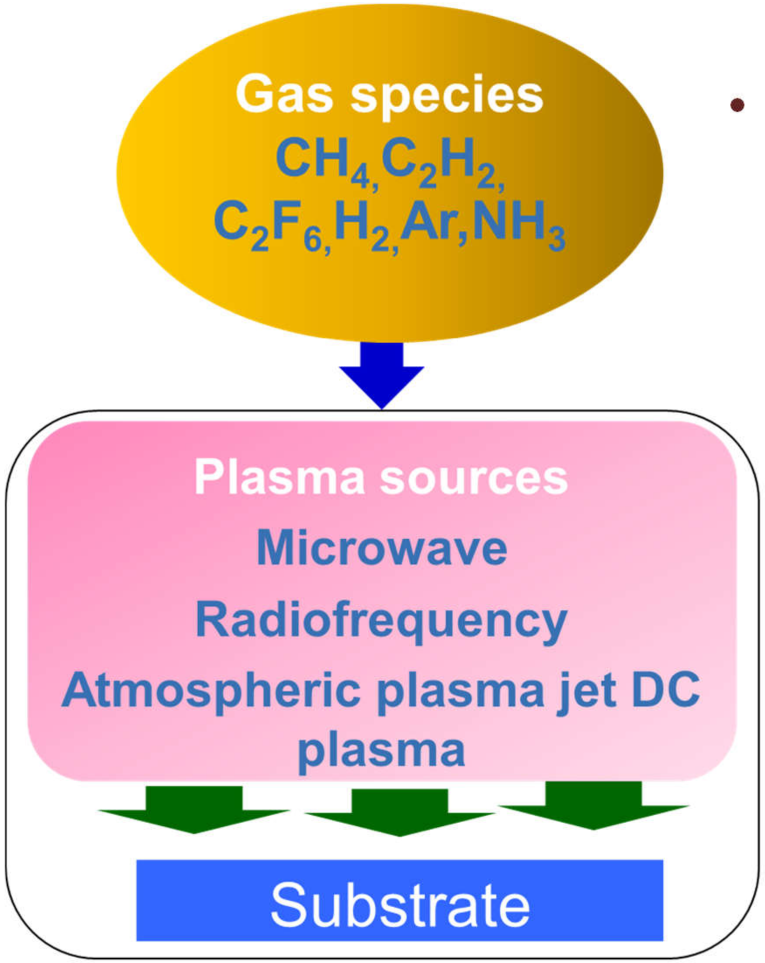
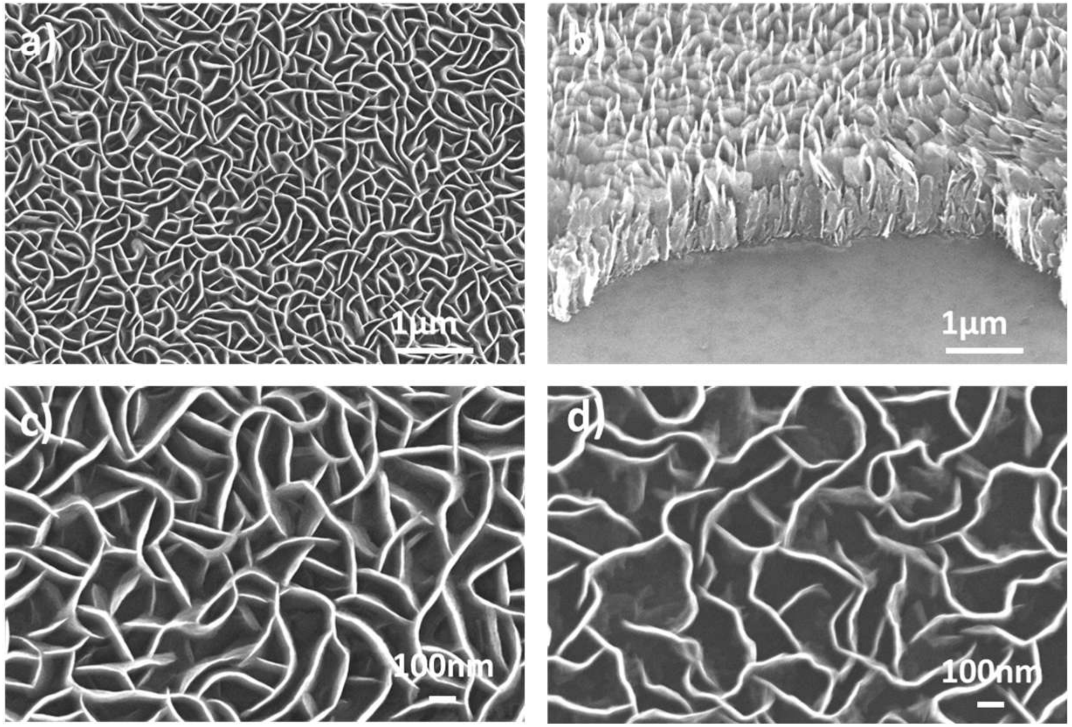
PECVD



- Vertical growth of CNWs (Currently reported maximum ~ 300nm)
- Atomically thin edges, controlled spacing, and excellent height uniformity



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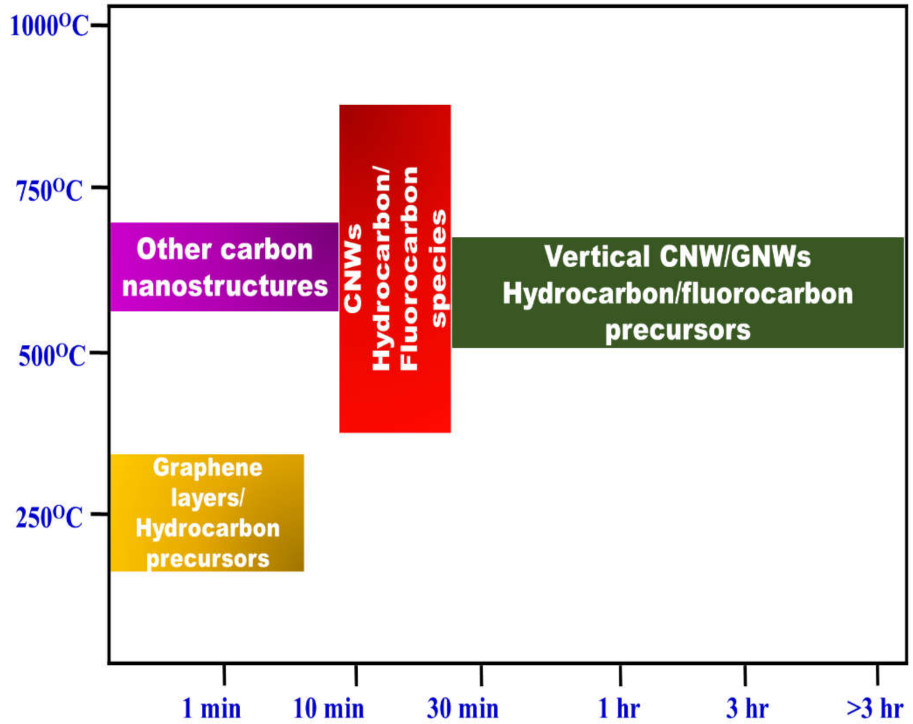
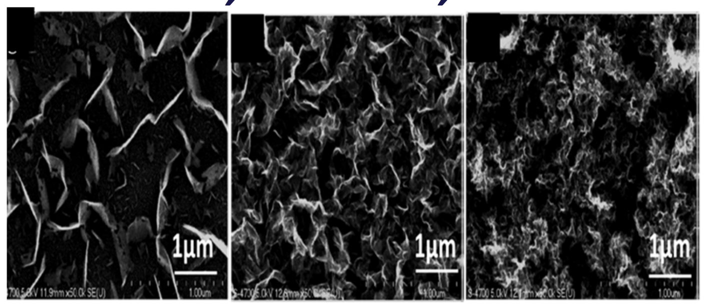
Mineo Hiramatsu, Masaru Hori, Carbon Nanowalls, Springer 2010

Substrate Temperature and Growth Time



N. M. Santhosh, G. Filipič, E. Tatarova, O. Baranov, H. Kondo, M. Sekine, M. Hori, K. Ostrikov, U. Cvelbar, Oriented Carbon Nanostructures by Plasma Processing: Recent Advances and Future Challenges, Micromachines. 9 (2018) 565. doi:10.3390/mi9110565.

Different growth temperatures: 630 °C, 730 °C, 830 °C.

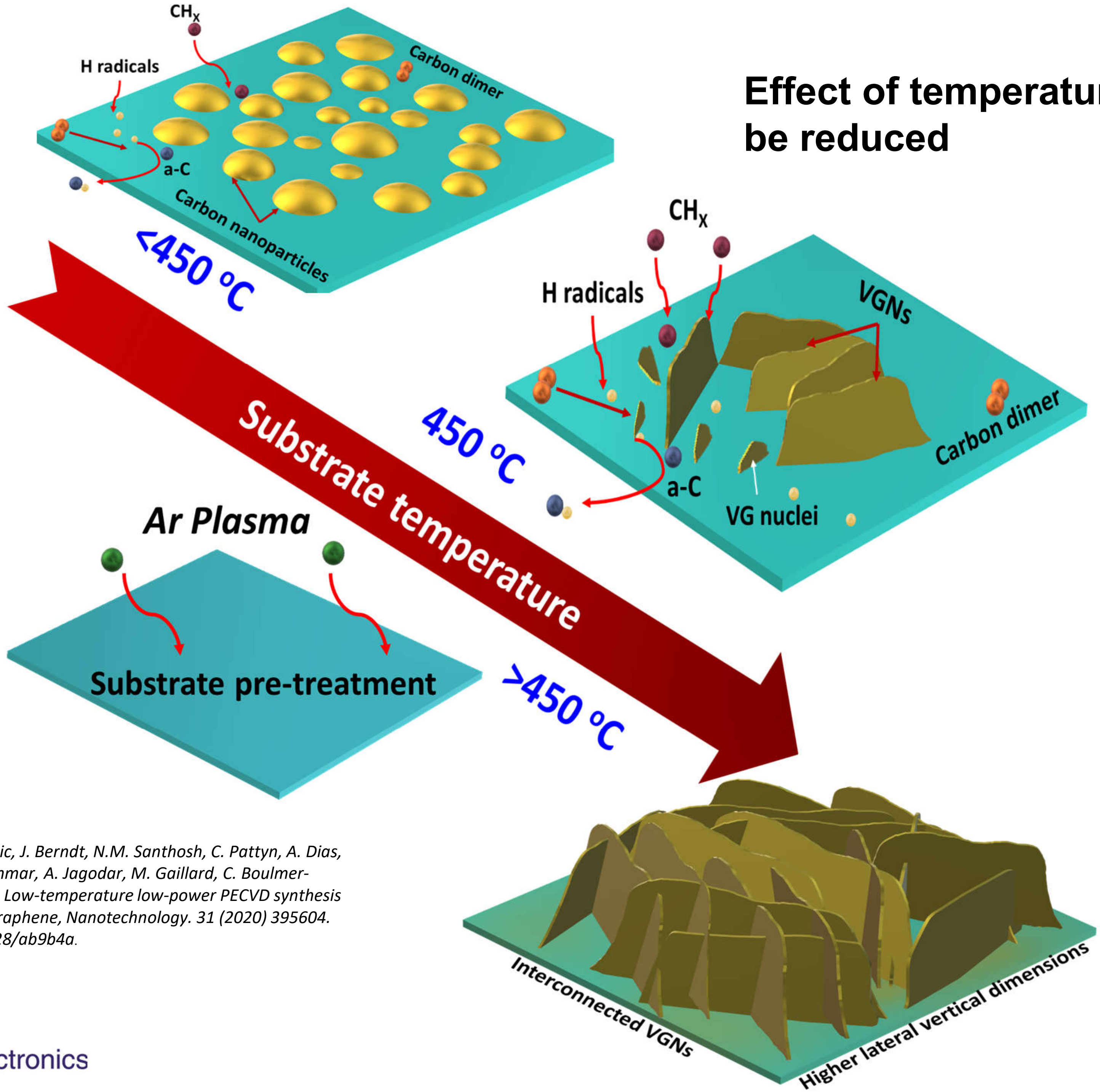


Wang, J.; Zhu, M.; Outlaw, R. A.; Zhao, X.; Manos, D. M.; Holloway, B. C., Carbon N. Y. ***2004****, 42, 2867–2872,.*

Attaining the growth of CNWs @ low-temperature and short-time period with high quality

Enhance the thermal stability of CNWs

Effect of temperature can be reduced



S. Hussain, E. Kovacevic, J. Berndt, N.M. Santhosh, C. Pattyn, A. Dias, T. Strunskus, M.-R. Ammar, A. Jagodar, M. Gaillard, C. Boulmer-Leborgne, U. Cvelbar, Low-temperature low-power PECVD synthesis of vertically aligned graphene, Nanotechnology. 31 (2020) 395604. doi:10.1088/1361-6528/ab9b4a.

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Effect of Pressure

Lower plasma pressure

- ✓ *Higher electron energy*
- ✓ *Increasing ionization rate*
- ✓ A low growth rate
- ✓ Higher vertical orientation

Higher plasma pressure

- ✓ Larger volume of feedstock gas input
- ✓ Electron energy decreased
- ✓ The massive production

Control the pressure, synthesize CNWs with uniform morphology, high orientation and larger interlayer spacing

Part 2 – SIMULATIONS FOR LARGE SCALE

Simulations - Formation of Vertically Oriented Graphenes: What are the Drivers of Growth?

We build a multi-scale, multi-factor model which was thoroughly verified by comparison with a large massive of experimental data to ensure a significant chemical and physical insight into the processes that determine nucleation, growth and structure formation of vertically-aligned graphenes from the case of plasma.

The leading role of surface diffusion fluxes, rather than direct influx from gas phase, was confirmed with **the ion bombardment being a key factor 'switching' the growth modes** by generating surface defects and hence, increasing the surface adsorption energy. Thus, the hydrocarbon radicals generated on a substrate due to the bombardment diffuse to the nanoflakes and catalyze the reactions, and *serve as the primary source of material to build the nanoflakes.*

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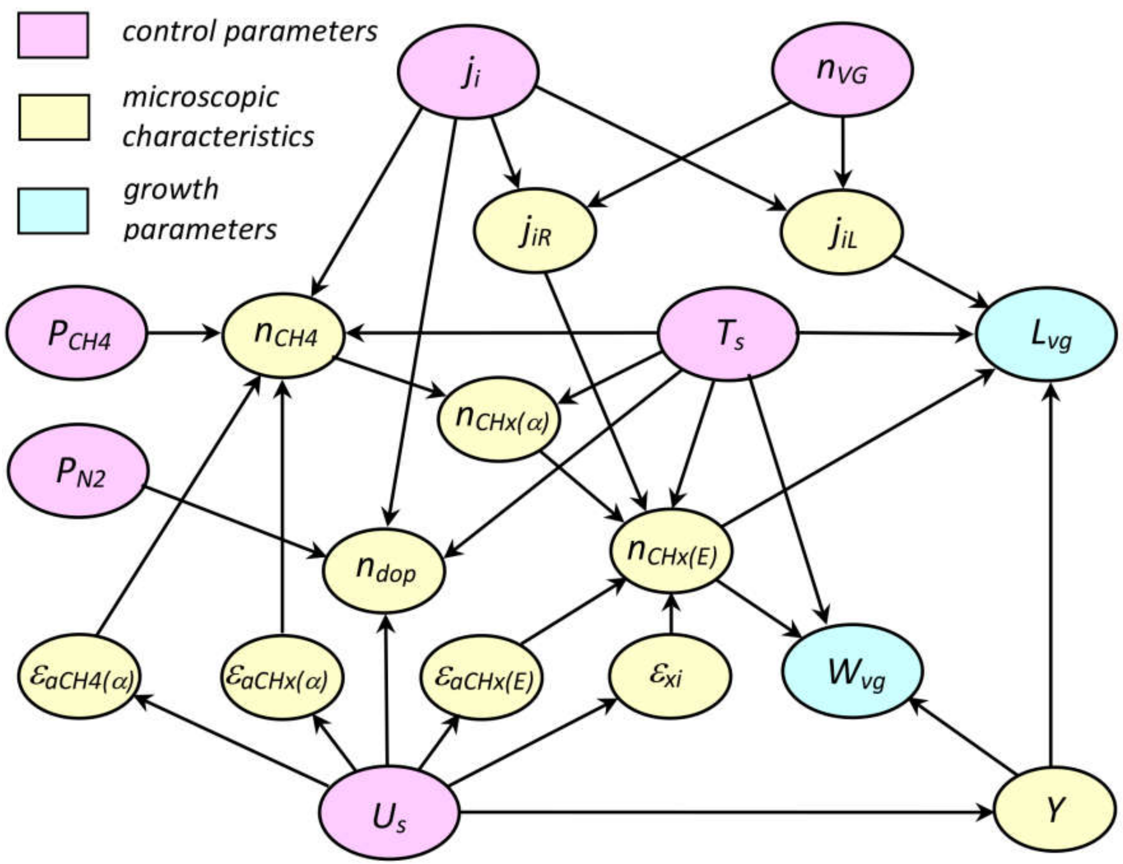
Developing a theoretical model for growth and doping of vertically oriented graphenes/N-graphene in the top-down approach.



L_{vg} – length (height) of a VG sheet

W_{vg} – half-width of the VG sheet

j_i – average density of ion current

j_{iR} – density of ion current to VG side edge

j_{iL} – density of ion current to VG top edge

T_s – temperature of the substrate

P_{CH4} – pressure of hydrocarbon gas

U_s – bias potential of the substrate

n_{VG} – surface density of VG sheets

n_{CH4} – surface density of adsorbed molecules of carbon precursor gas

$n_{CHx(\alpha)}$, $n_{CHx(E)}$ – surface densities of radicals on the substrate and VG edge

$\varepsilon_{aCH4(\alpha)}$ – energy of adsorption of carbon precursor on the substrate

$\varepsilon_{aCHx(\alpha)}$, $\varepsilon_{aCHx(E)}$ – energies of activation of carbon radicals diffusion along the substrate and VG edge

ε_{xi} – energy gained at the ion bombardment

Y – sputter yield

Schematic of the dependencies of the growth characteristics on the control parameters through the microscopic quantities.

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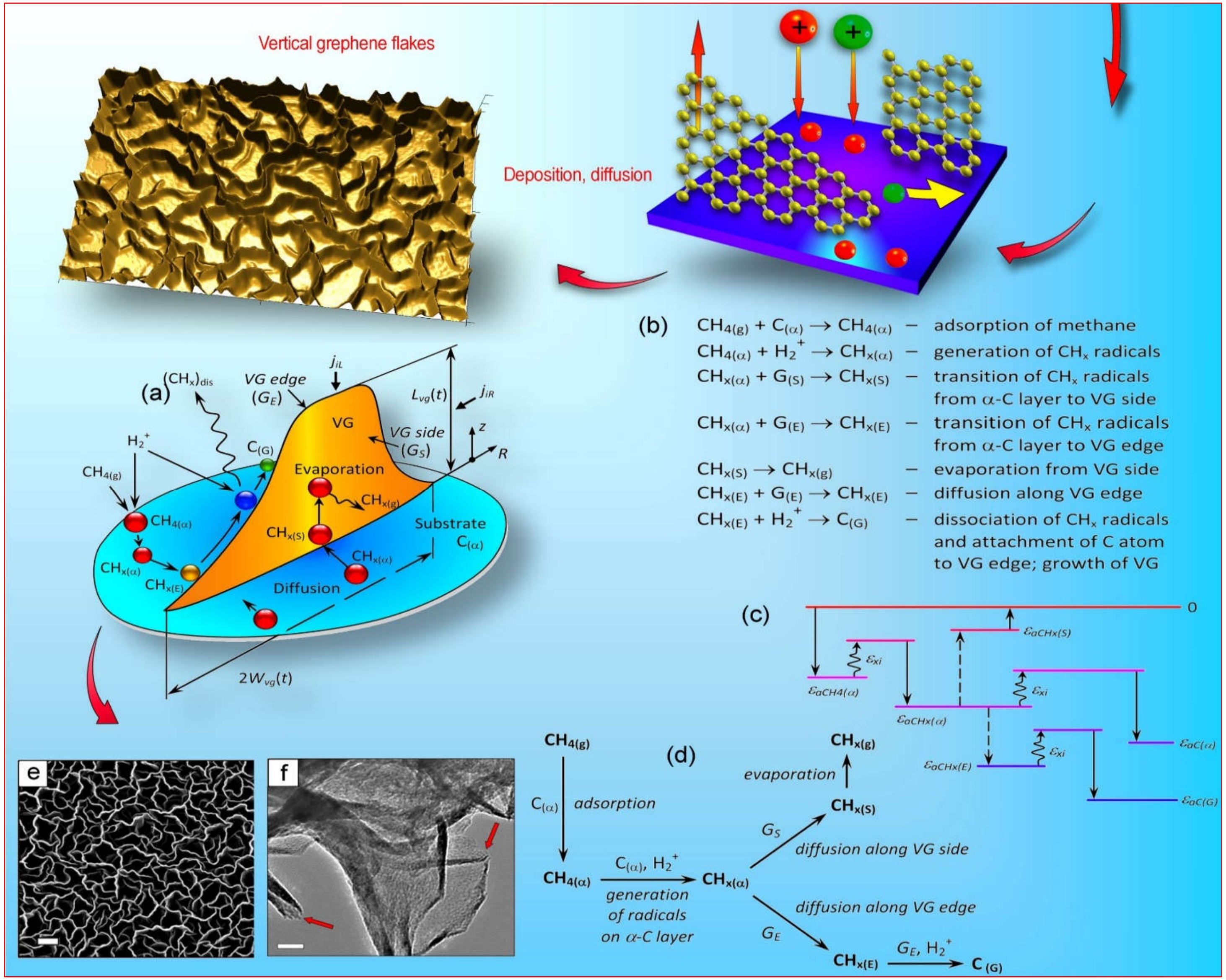

The prepared substrates are loaded into the chamber of plasma reactor where the nanoflakes are **nucleated on catalyst particles and then grow in the ion and atom flux**. Schematic of the mechanisms and reactions involved in vertical graphene growth. Motion of species involved into the reactions about the surface of growing graphene flake (a); list of chemical reactions taken into account in the model (b); schematic of the reactions (c); and diagram of the energy levels (d). Substrate may be externally heated by the use of heating coil, or heated directly by the plasma.

BARANOV, Oleg B., LEVCHENKO, Igor, XU, S. F., LIM, J. W. M., CVELBAR, Uroš, BAZAKA, Kateryna. Formation of vertically oriented graphenes : what are the key drivers of growth?. 2D materials, ISSN 2053-1583, 2018, vol. 5, no. 4, str. 044002-1-044002-13, doi: [10.1088/2053-1583/aad2bc](https://doi.org/10.1088/2053-1583/aad2bc).

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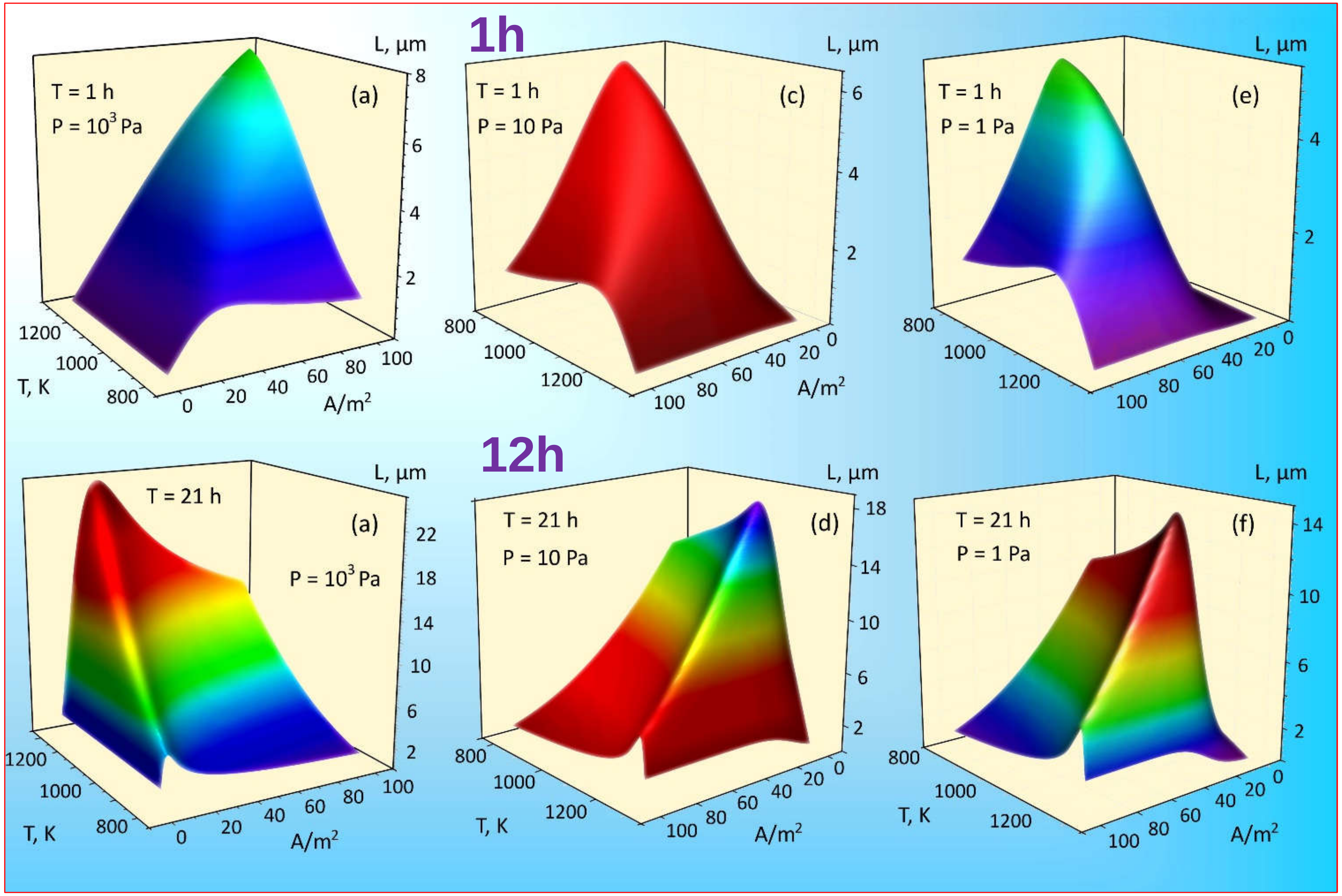
Nanoflake length



Big data", i.e. large volume of information obtained from the multiscale multifactor model allows comprehensive analyzation of the graphene formation and growth as a function of all essential parameters and processes in plasma.

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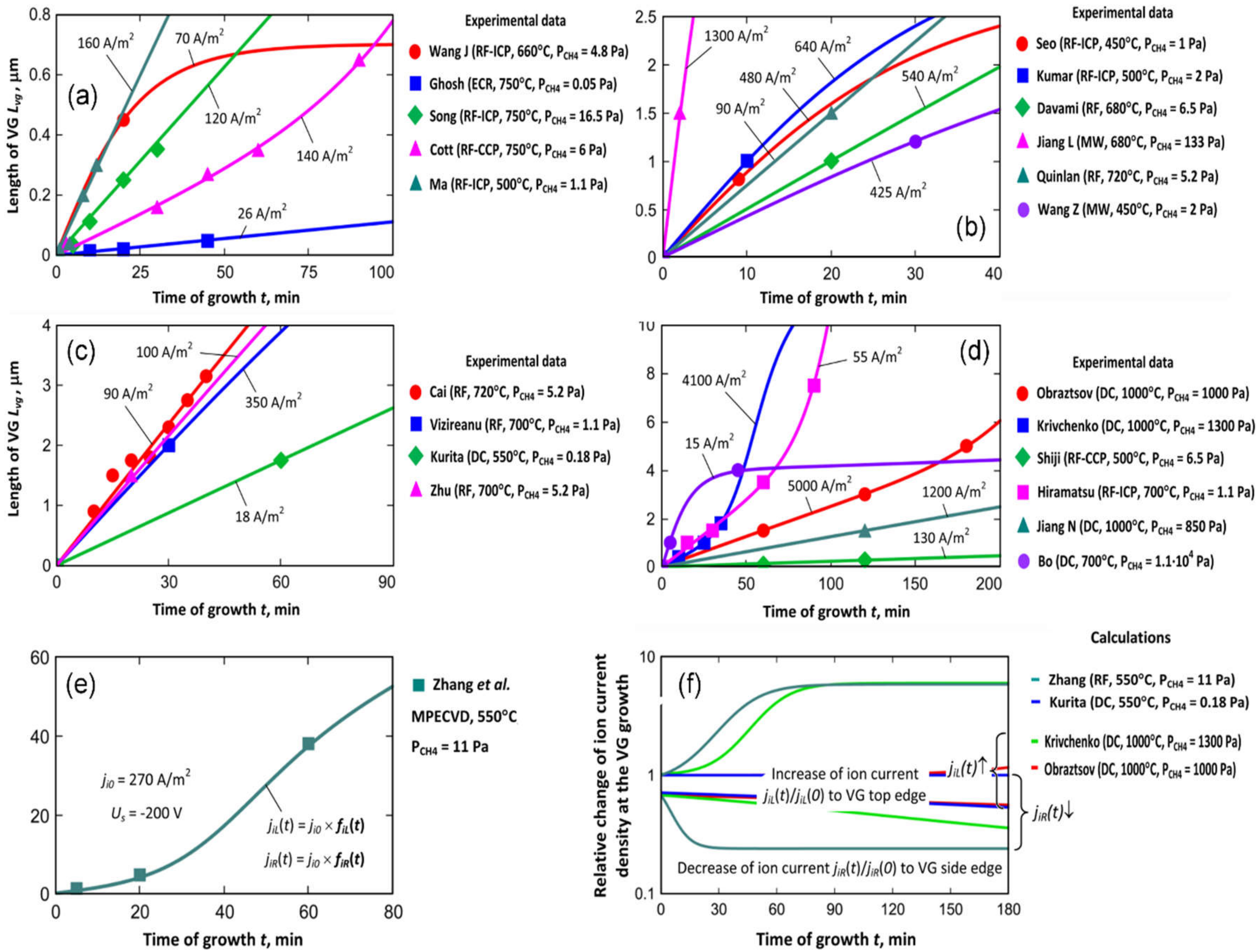
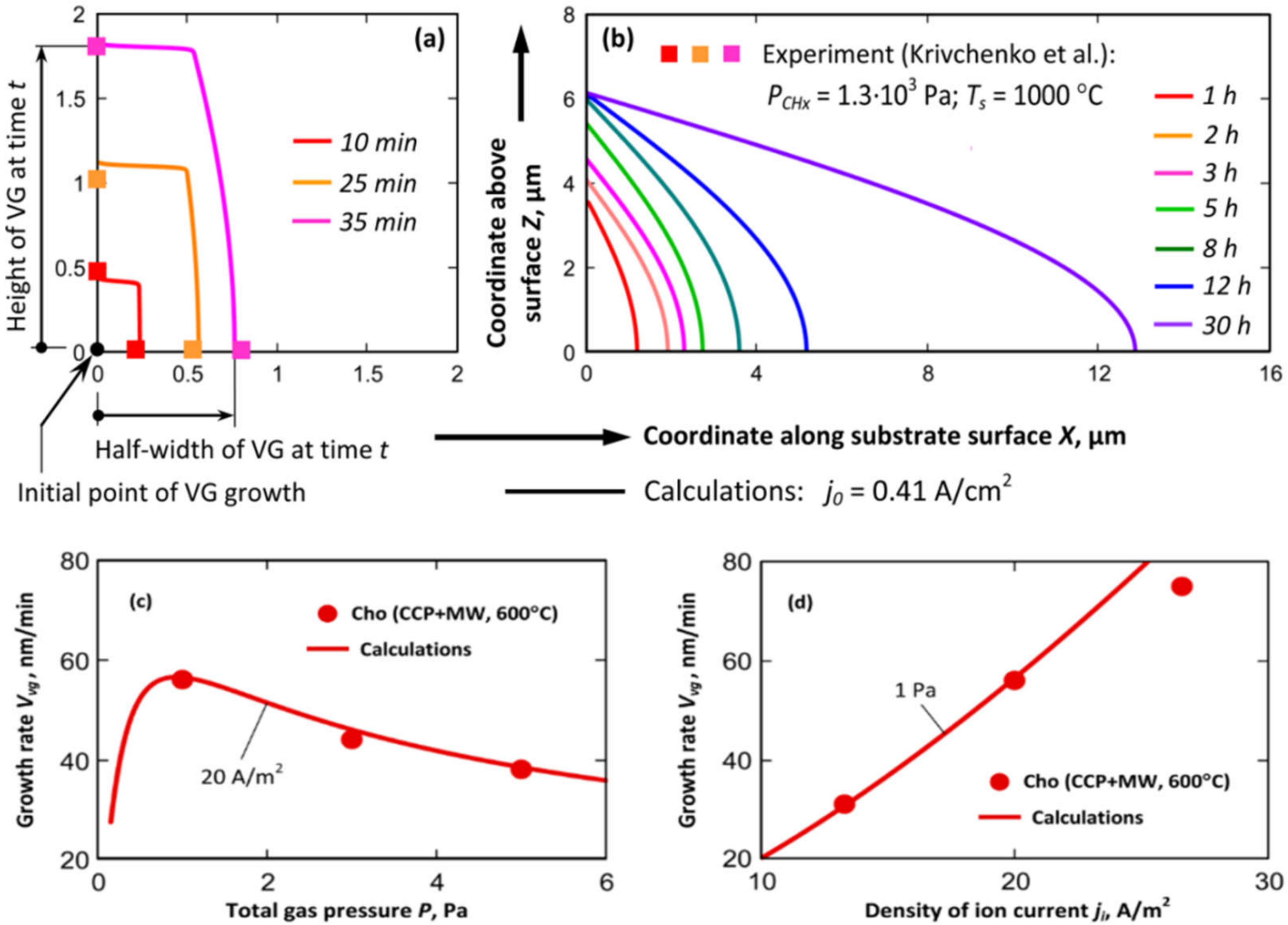
Growth kinetics



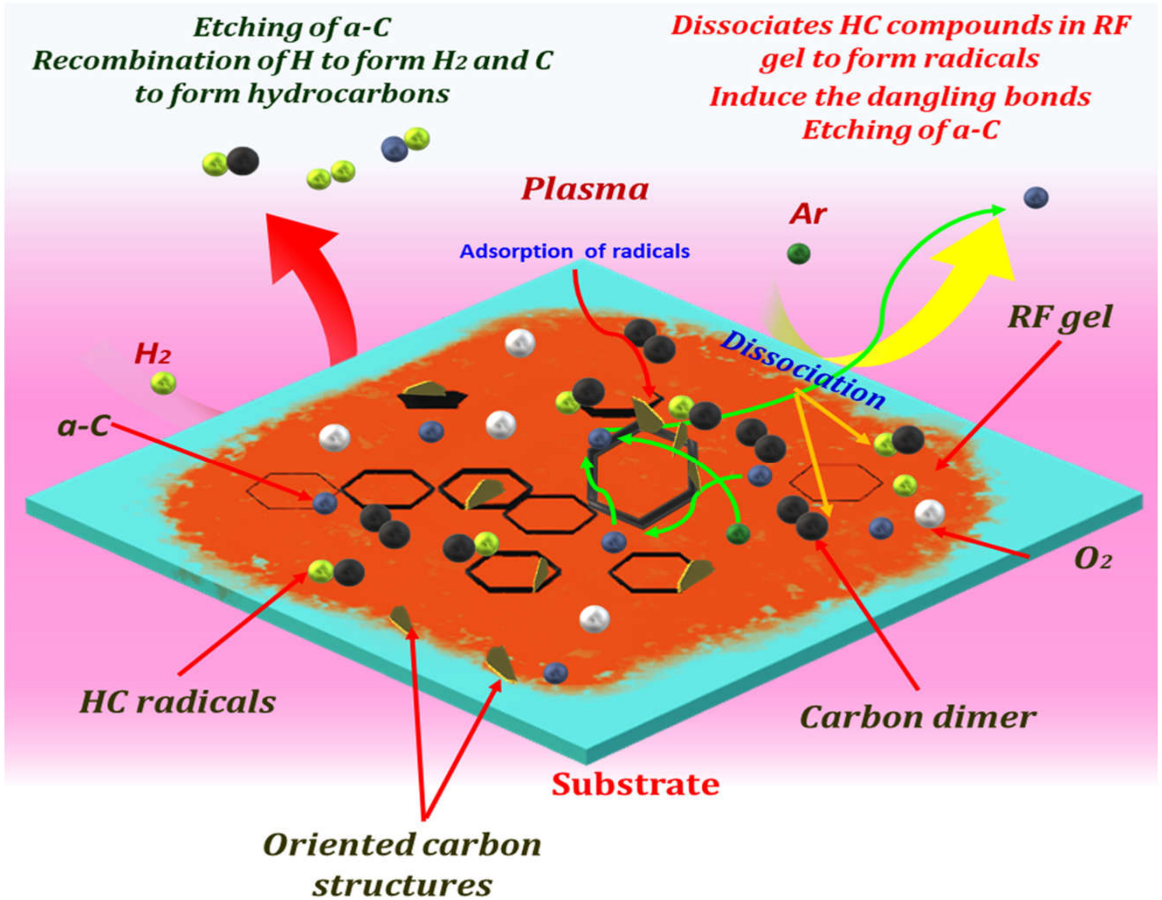
GNF length on time under various growth conditions. j_{iL} was considered a parameter, and calculated for various types of plasma discharge based on the experimental data. Comparison with experimental data shows that the ion bombardment results in changing the ion-stimulating diffusion to ion mixing mode. Non-linear growth with saturation is explained by a dependence of the ion current densities j_{iL} and j_{iR} on time for the particular experiment



Time evolution of a GNF shape at j_0 = 0.41 A/m^2, PCHx = 1300 Pa, Ts = 1000 °C. The GNF shape evolves **from a rectangular with a height to width ratio of about unity at the initial stages of growth** (a), to a ribbon-like structure of limited height (~6 µm) (b). Experimental bars correspond to the results obtained by Krivchenko et al.[18] In the calculations the non-liner fit of *jiLjiR* is assumed. (c) GNF growth rate on density of ion current, total gas pressure is a parameter.

Part 3 – EXPERIMENTS Bottom-up

Mechanism of growth



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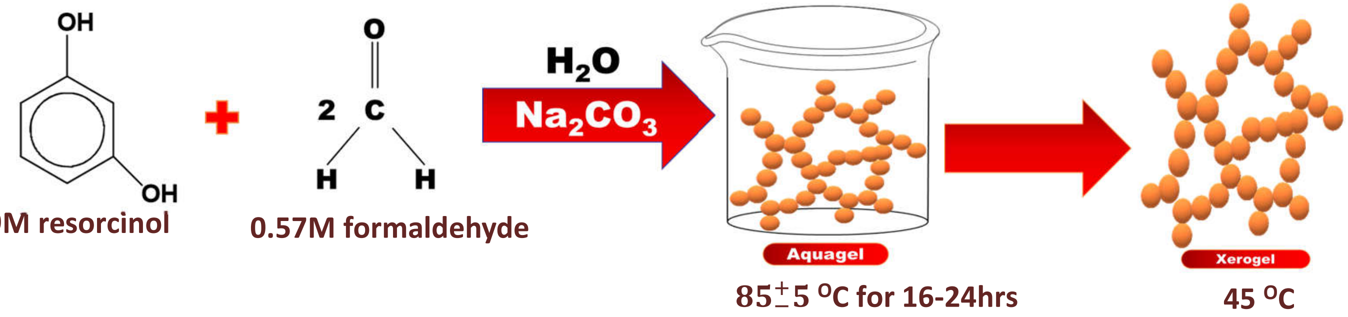
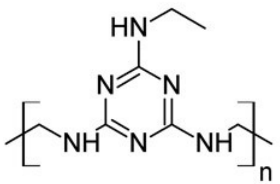
Santhosh, N. M.; Vasudevan, A.; Jurov, A.; Filipič, G.; Zavašnik, J.; Cvelbar, U. Oriented Carbon Nanostructures from Plasma Reformed Resorcinol-Formaldehyde Polymer Gels for Gas Sensor Applications. Nanomaterials ***2020****, doi:10.3390/nano10091704.*

Experimental

Gel preparation



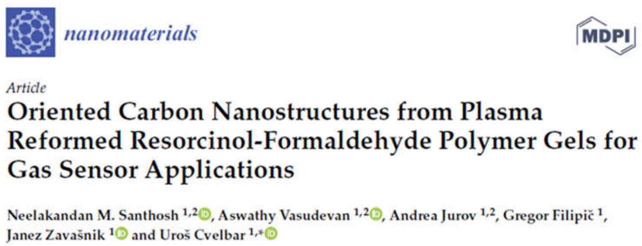


Melamine formaldehyde

Solution changed color upon curing from clear to yellow to orange to deep red

Plasma etching

- *Radio frequency inductively coupled plasma (RFICP)*
- Reactive gases: *Argon* and *hydrogen* in a different ration
- Different times


nanomaterials MDPI

Article

Oriented Carbon Nanostructures from Plasma Reformed Resorcinol-Formaldehyde Polymer Gels for Gas Sensor Applications

Neelakandan M. Santhosh [1,2], Aswathy Vasudevan [1,2], Andrea Jurov [1,2], Gregor Filipič [1], Janez Zavašnik [1] and Uroš Cvelbar [1,*]

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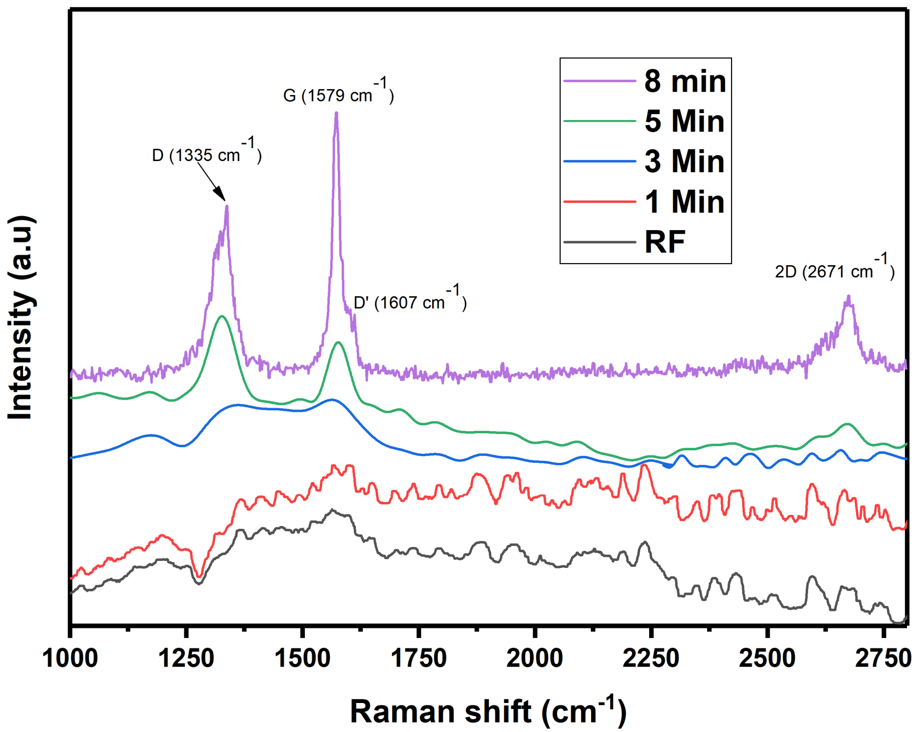
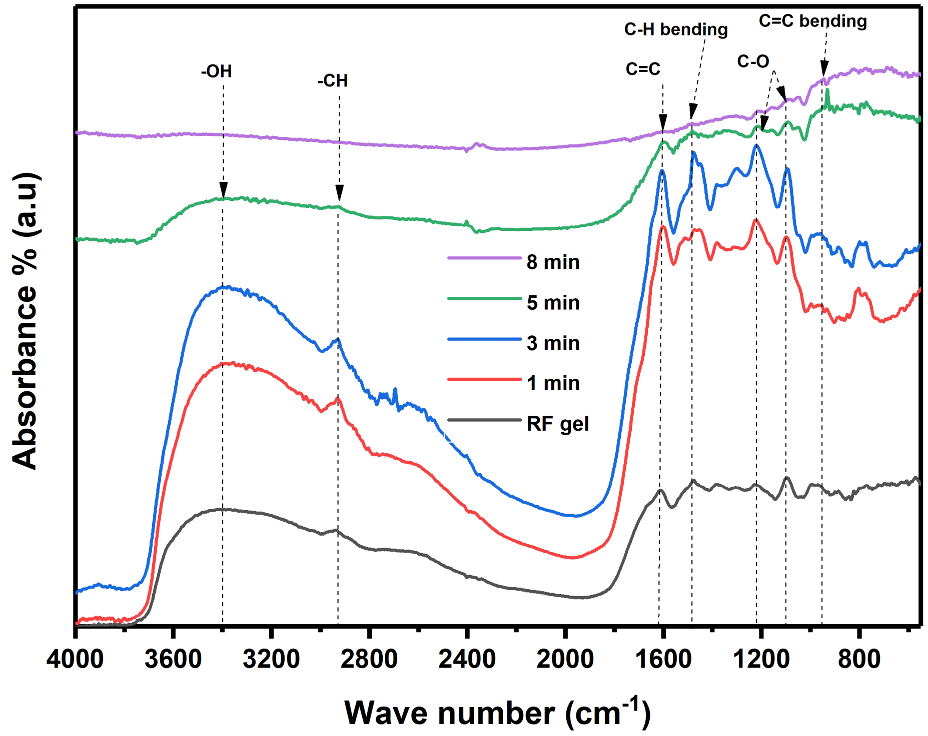
Raman and FTIR Analysis





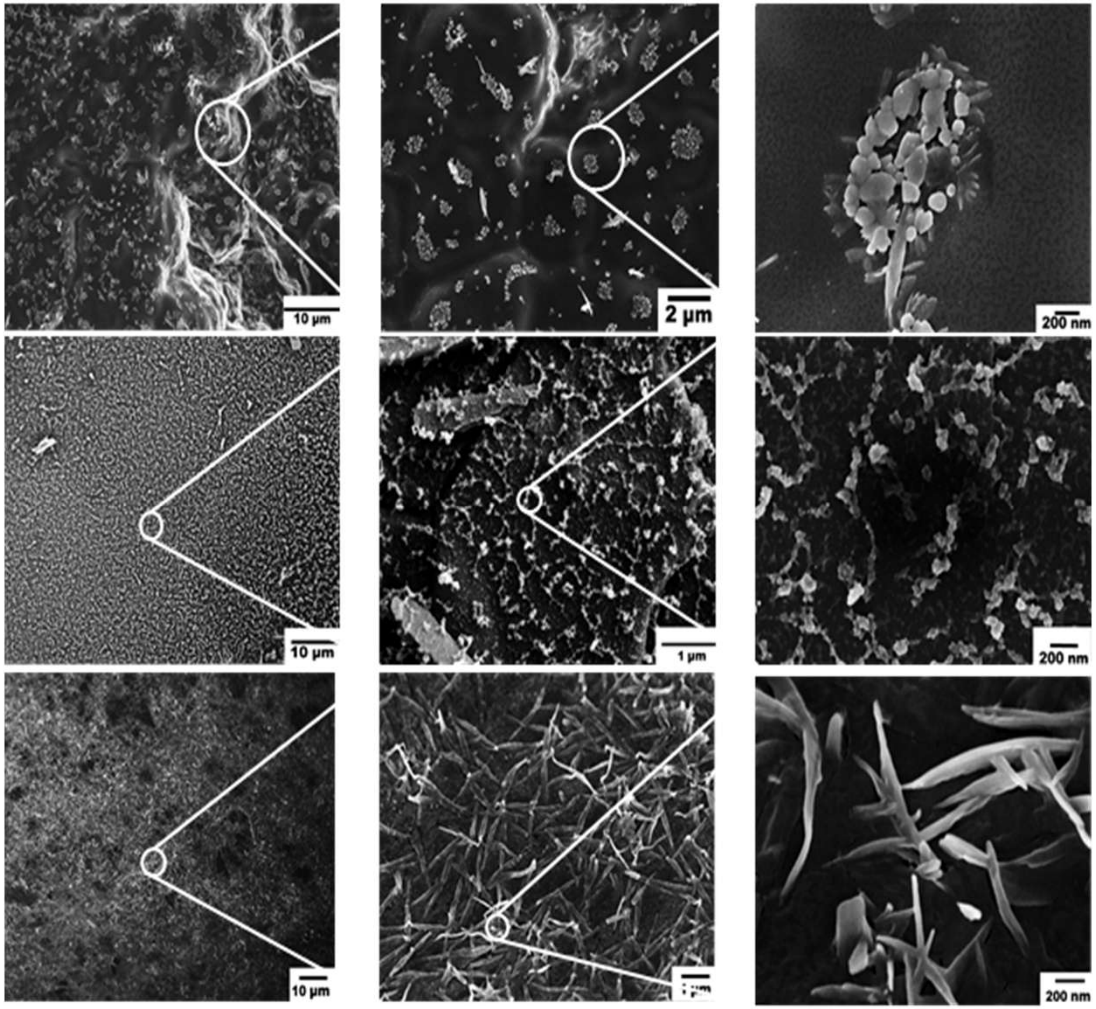
Carbon Nanostructure; Power: 250W; Time: 1-8 min; and Ar:H_2 : 100:50 sccm

SEM images

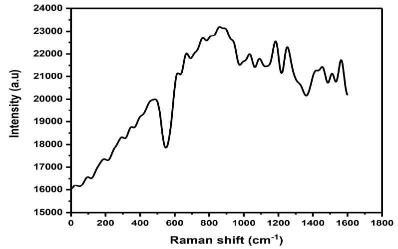
3 Min

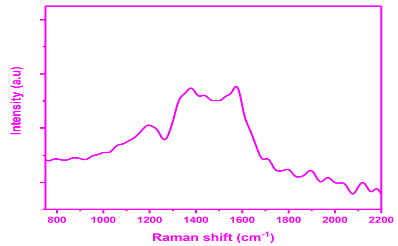
5 Min

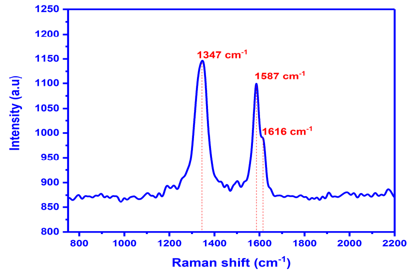
8 Min



Raman Spectrum Analysis







„Synthesis of 2D vertical graphenes"
plasma-assisted synthesis of vertically aligned carbon nanowalls (multilayers graphenes) on substrates by using gel reduction method was achived.

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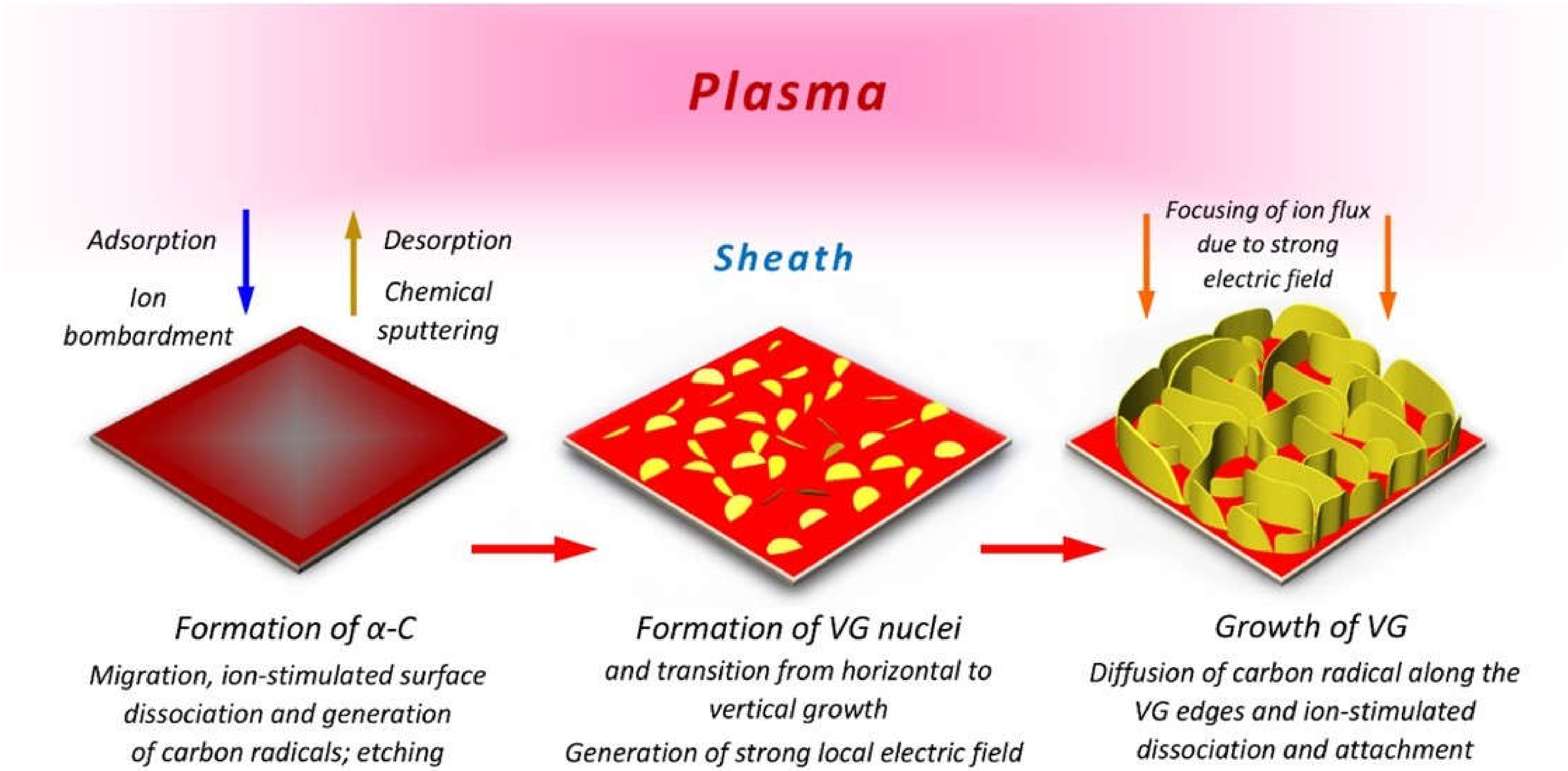
Part 4 – EXPERIMENTS Top-down



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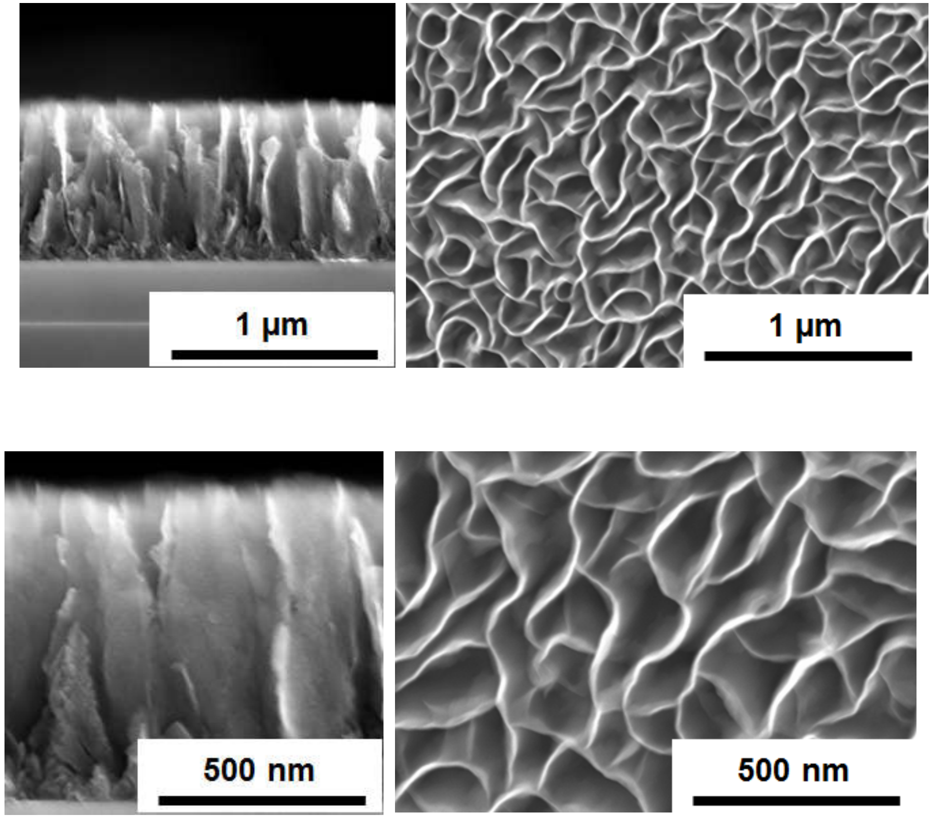
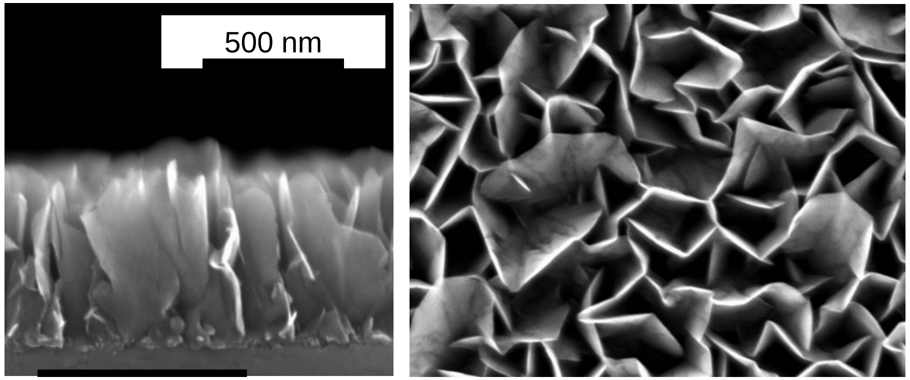
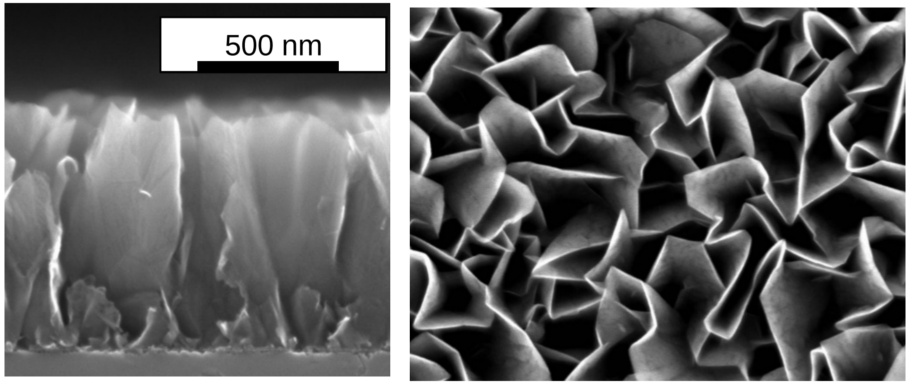
CH-CNWs SEM images



CF-CNWs 1



CF-CNWs 2



RI-PECVD system
(Radical Injection Plasma Enhanced CVD)
Nagoya

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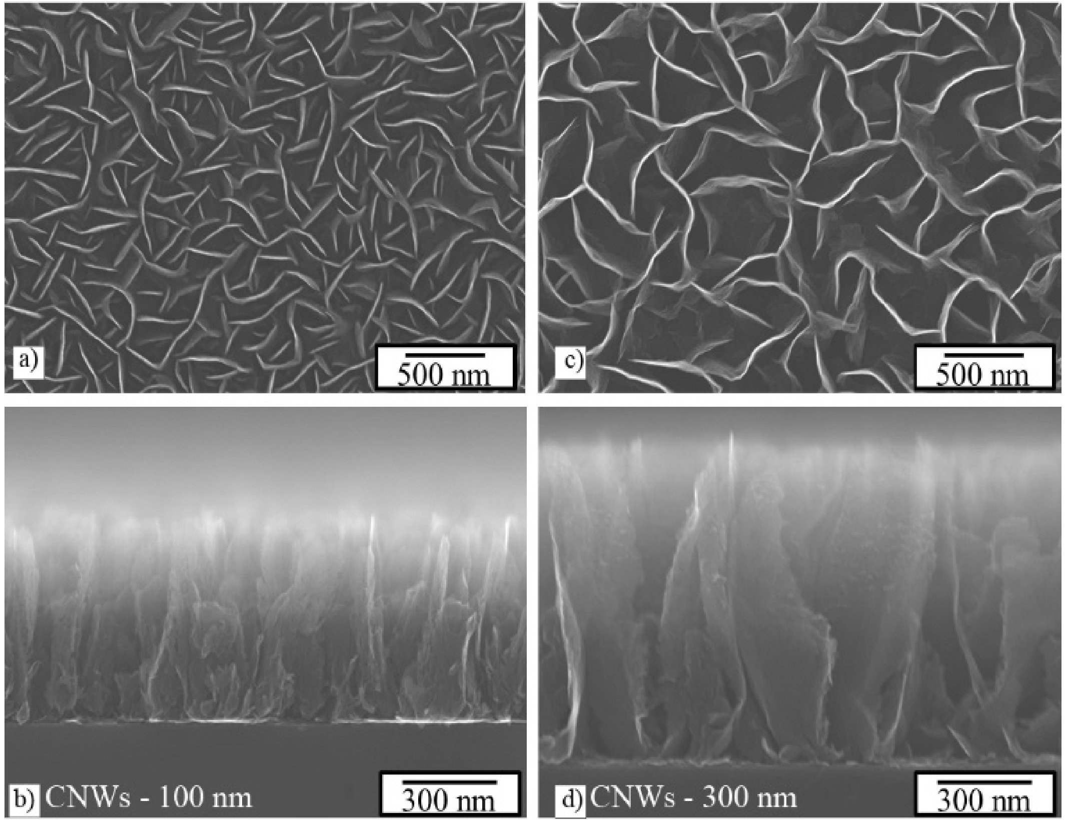
F atoms from C2F6/H2 plasma might **act as a dopant** at the graphene edges. Consequently, electrical properties could be controlled while maintaining the crystal quality and chemical bonding state.

Different spacing between CNW

Process conditions and results of analyses of both principal tested CNWs (100 nm) and CNWs (300 nm).

Average gap between each CNWs [nm]	100	300
Average height of CNWs [nm]	650	970
Conductivity [S/cm]	38	76
Process pressure [Pa]	1	5
Substrate temperature [°C]	600	600
SWP power [W]	400	400
CCP power [W]	100	500
H_2 [sccm]:CH_4 [sccm]	50:100	50:100
Growth time [min]	60	10



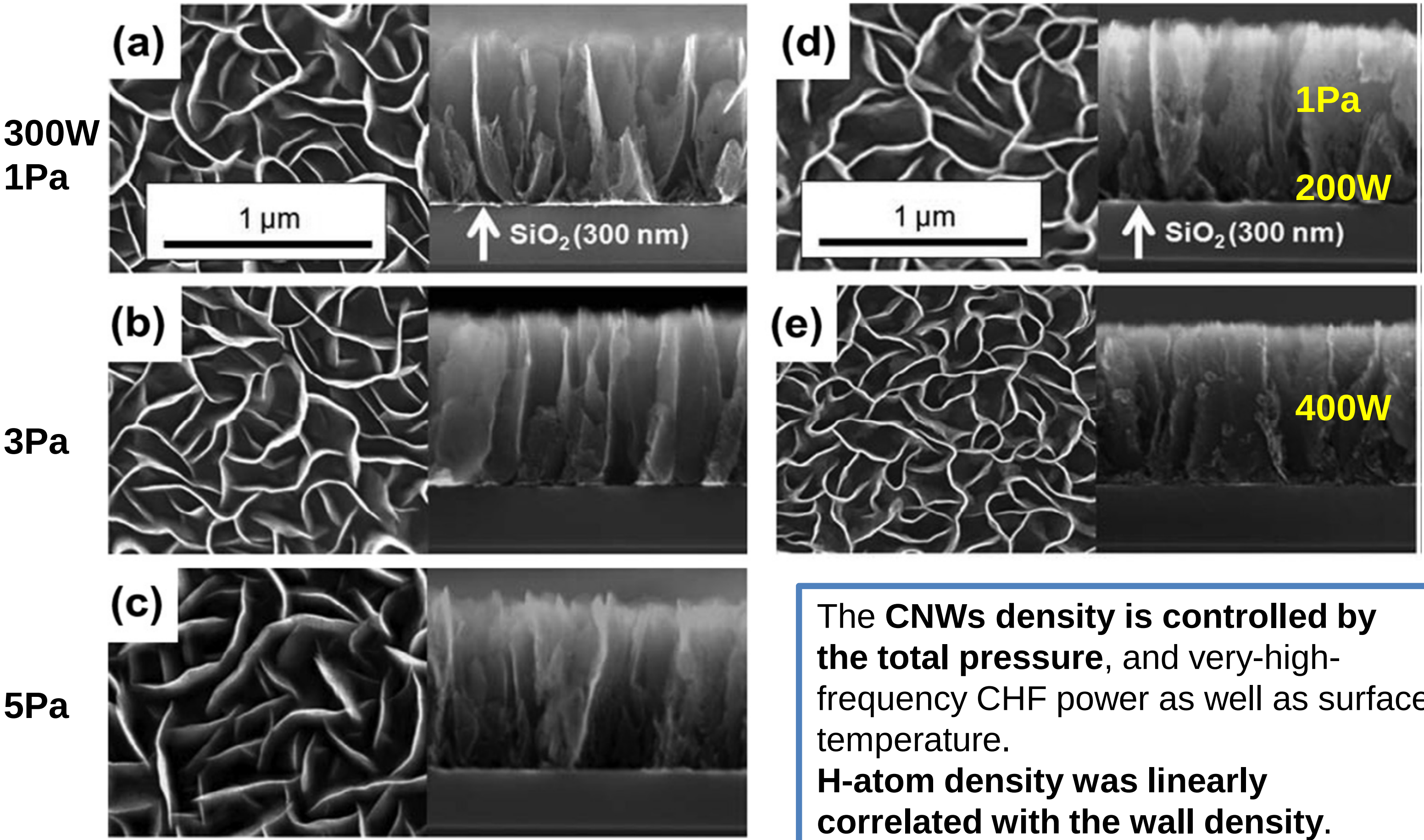
I_D/I_G, $I_{D'}/I_G$, I_{2D}/I_G ratios and the position of peaks of Raman spectra for both tested CNWs.

	$\frac{I_D}{I_G}$	$\frac{I_{D'}}{I_G}$	$\frac{I_{2D}}{I_G}$	I_D [cm^{-1}]	I_G [cm^{-1}]	$I_{D'}$ [cm^{-1}]	I_{2D} [cm^{-1}]
100 nm	2.2	0.91	0.40	1357	1597	1624	2693
300 nm	2.0	0.84	0.45	1334	1581	1607	2684

→ No obvious difference in material structure.

No change in the crystal quality (Raman) and the chemical bonding states (XPS) is observed between CNWs

Growth of different CNW in CH4/H2



The **CNWs density is controlled by the total pressure**, and very-high-frequency CHF power as well as surface temperature.
H-atom density was linearly correlated with the wall density.

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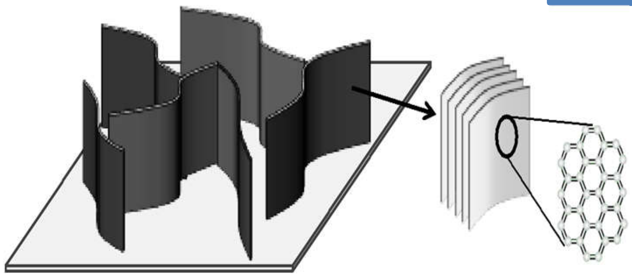
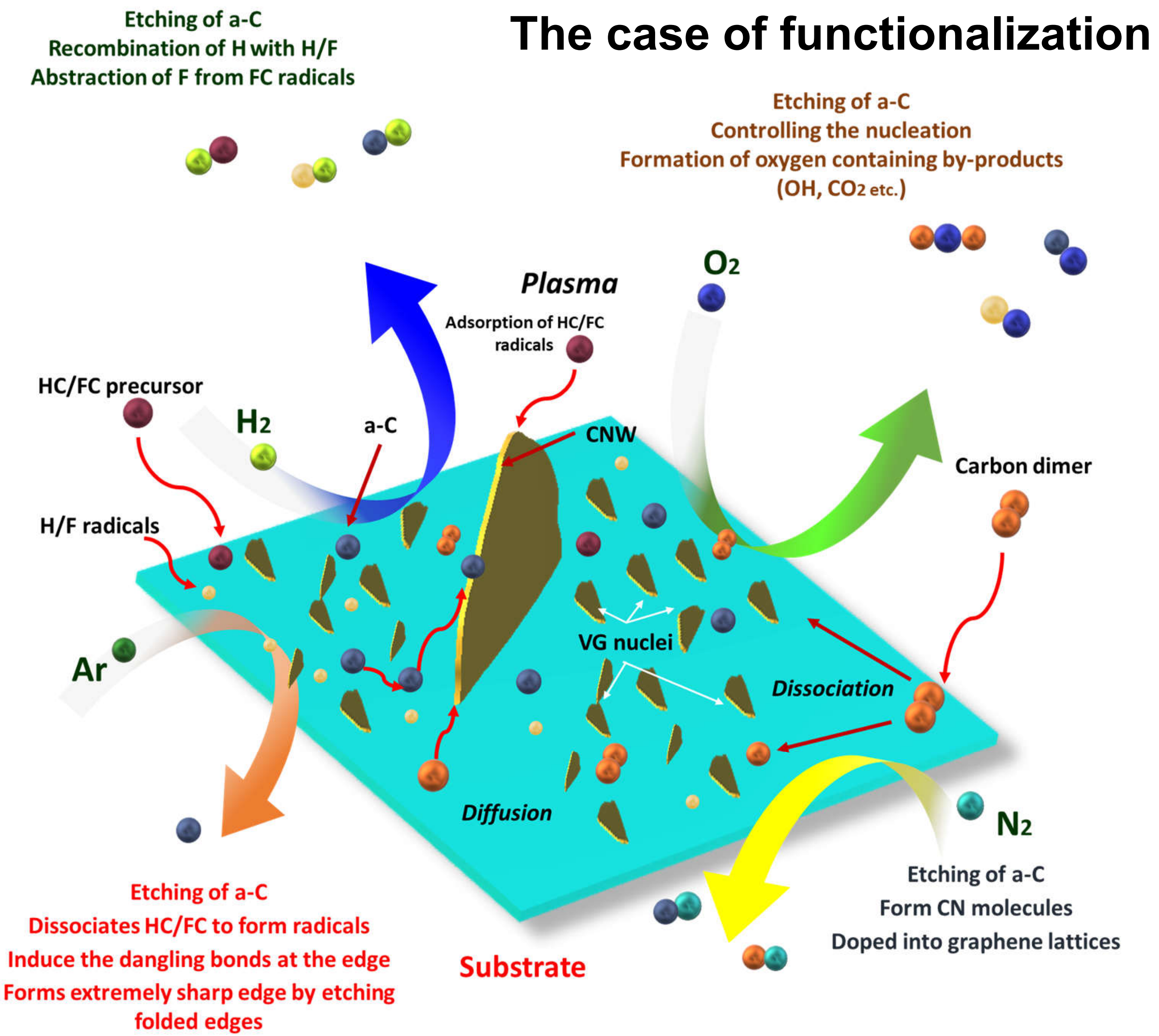


*M. Hiramatsu, H. Kondo, M. Hori, in New Prog. Graphene Res., InTech, **2013**, p. 13.*

Part 5 – Beyond Graphene and N-Doping

Hydrogen Plasma treatment Hydrocarbon precursors	CNWs FLGs, Petal like carbon nanostructures	•H radicals creates sp^2 bonded carbon at the surfaces to form continuous sp^2 network and etch away the disordered amorphous carbon •Results in the formation of high quality 2D carbon nanostructures
Oxygen plasma treatment Hydrocarbon/ Fluorocarbon precursor	CNWs, FLGs Single nucleated CNWs	•Trigonal bond of carbon at the edges with defects react with oxygen and forms volatile by-products and control the nucleation reaction •This enables to synthesize carbon materials that have larger crystallite sizes, higher crystallite alignment, and higher purity
Argon plasma treatment Hydrocarbon/ Fluorocarbon precursor	CNWs, FLGs, Vertical grown CNs	•Ar ions enhances the surface reaction in the growth phase and induce the dangling bonds between the surface results in nucleation sites •Presence of Ar helps to remove the folded edges of the CNWs and forms extremely sharp edge •Enhances the geometrical factor and field emission properties
Nitrogen plasma treatment Hydrocarbon/Fluorocarbon precursor	CNWs, FLGs	•N atoms incorporated into the defects and disordered grain boundaries •Results in the increase in domain size, improvement in crystallinity, enhancement in surface conductivity
Other plasmas Fluorine, Chlorine, Boron	Doped few-layers of graphene sheets	•In most of all these plasmas nucleation enhanced by the presence of Ar •Doping of substitute atom varies the wettability, optical properties, surface area and electrical properties

The case of functionalization



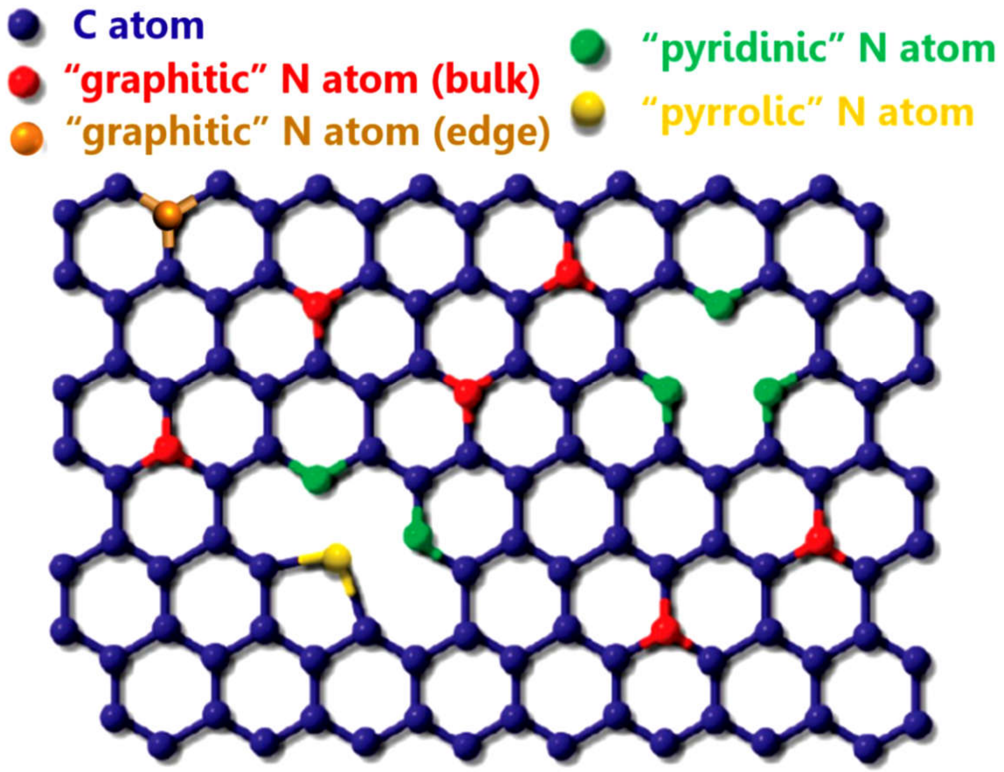
Running multiple processes on surface leading to:

- Structural defects
- Etching
- Doping
- ..

Extrinsic Defects: N-Doped graphene

"Adsorption of nitrogen to the graphene lattice or substitution of C atom by nitrogen"

- **Pyridinic N:** on edges, N- sp^3
- **Pyrrolic N:** five membered ring structure with unshared electron pair, N-sp^2
- **Graphitic N:** C substituted by N in graphene basal plane, N-sp^2
- **Amine**
- **N-oxides of pyridinic-N**



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Building N-graphene:

- **In-situ process**
  - During the synthesis of graphene structures.
  - Nitrogen incorporation throughout the bulk material.
- **Ex-situ process**
  - Post-treatment on the graphene structures.
  - Nitrogen incorporation mostly on the surface.

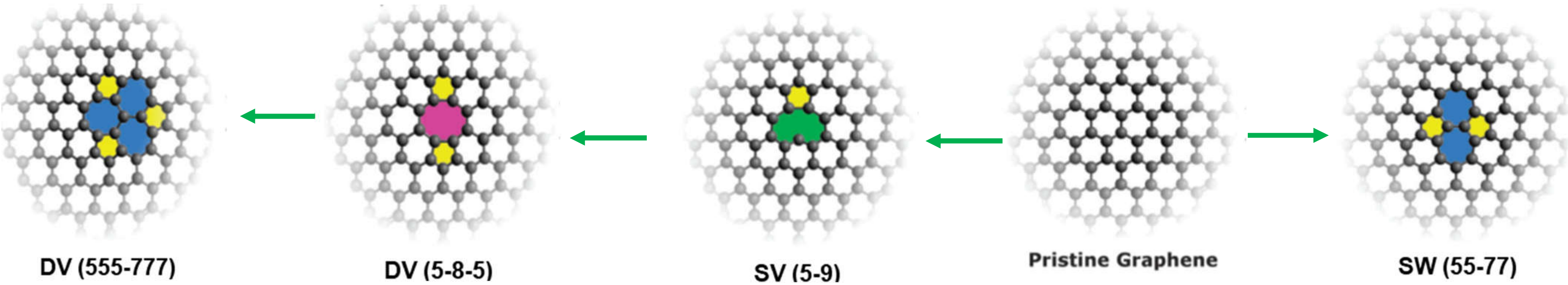
Thermal annealing

- Post-treatment at temperature ~ 600-1000 ^{O}C
- Hard to control the bonding environments
- Low-concentration of incorporation due to Lower defect generation and high temperature

Plasma post-treatment

- Nitrogen containing plasma
- Control over the bonding configurations
- High-concentration of incorporation due to simultaneous defect generation and incorporation

Structural defects in graphene and interaction with N-atom



DV: Double vacancy defect **SV: Single vacancy defect** **SW: Stone-Wales defect**

- **Graphitic-N** (sp^2 C-N) : Substitutes the missing carbon atom in SV or DV defects
- **Pyridinic-N** (sp^2 C-N) : Situated at the edges of graphene and at DV with a SV
- **Pyrrolic-N** (sp^3 C-N) : Situated at the edges of graphene and at DV after longer plasma exposure

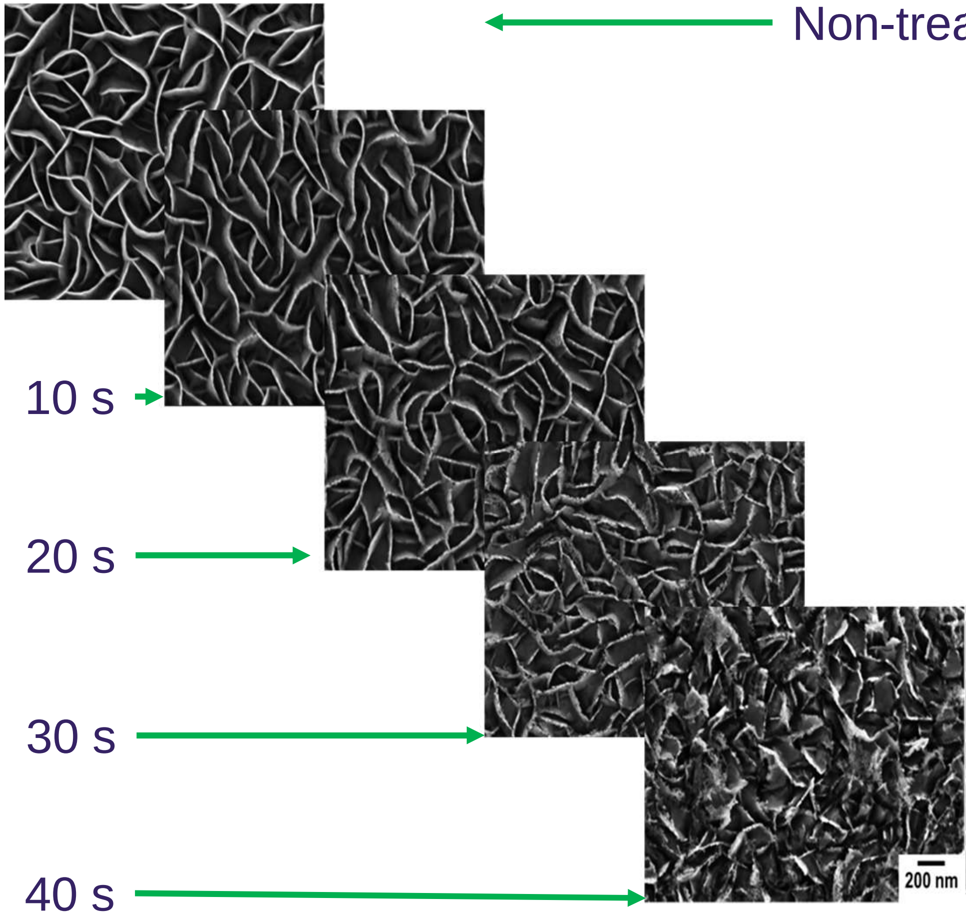
S. T. Skowron, I. V. Lebedeva, A. M. Popov, E. Bichoutskaia, Chem. Soc. Rev. ***2015****, DOI 10.1039/c4cs00499j.*

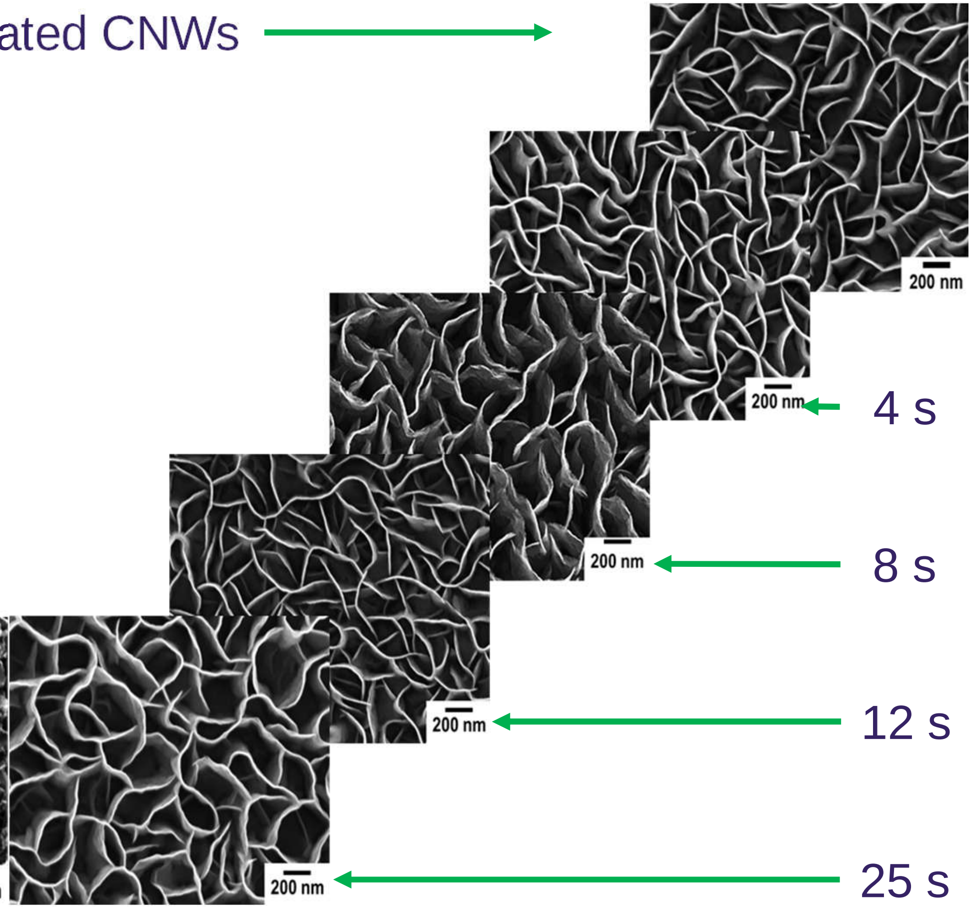
Surface morphology

N_2 Plasma

NH_3 plasma

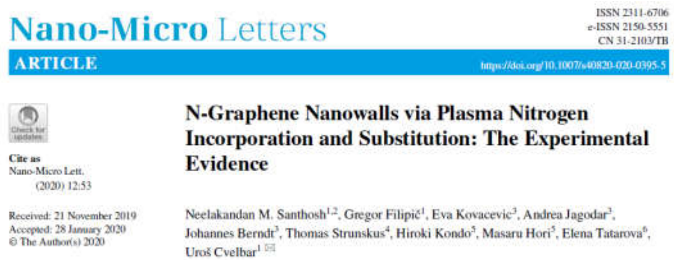
Non-treated CNWs





10 s
20 s
30 s
40 s

4 s
8 s
12 s
25 s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N-Graphene Nanowalls via Plasma Nitrogen Incorporation and Substitution: The Experimental Evidence

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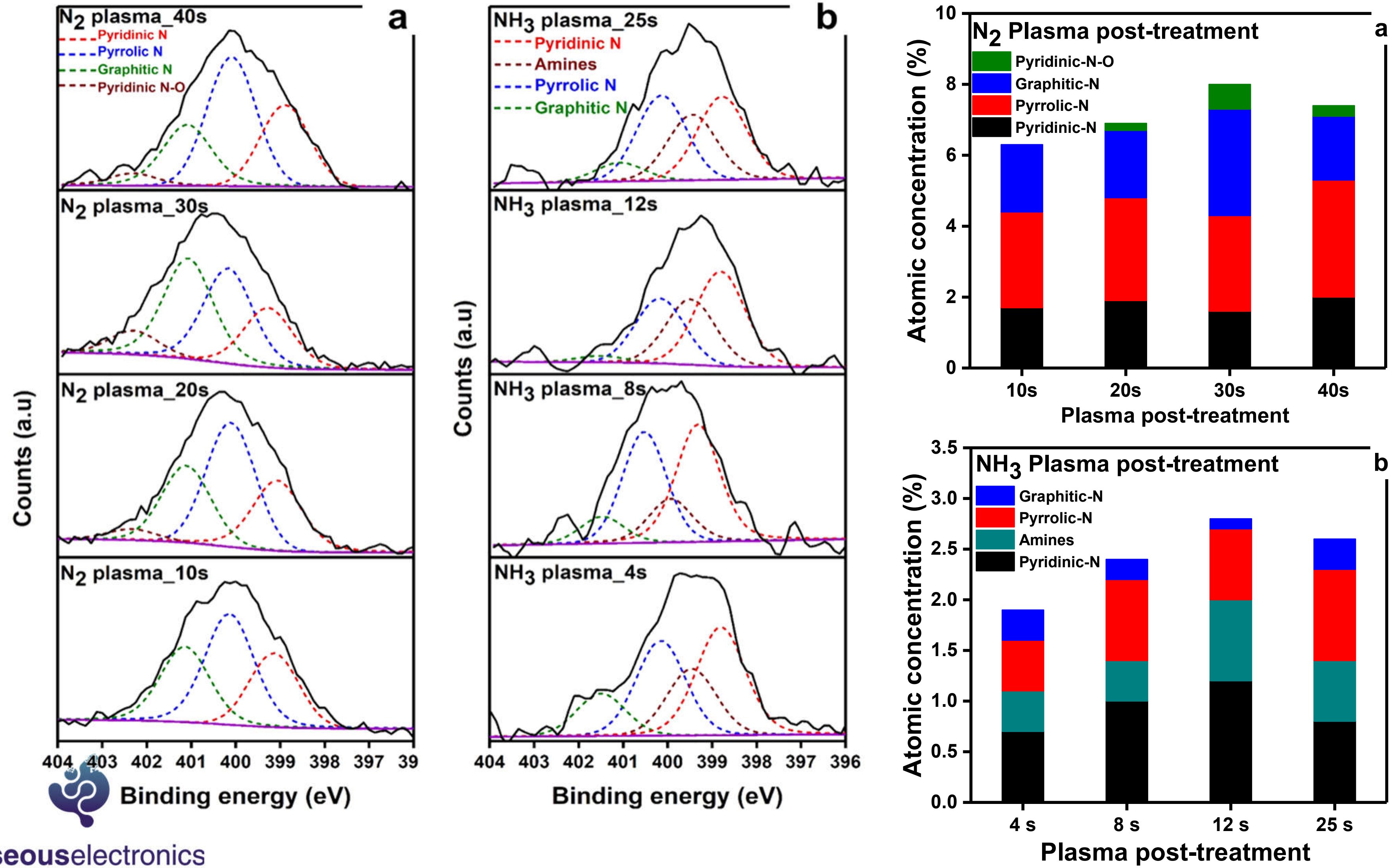
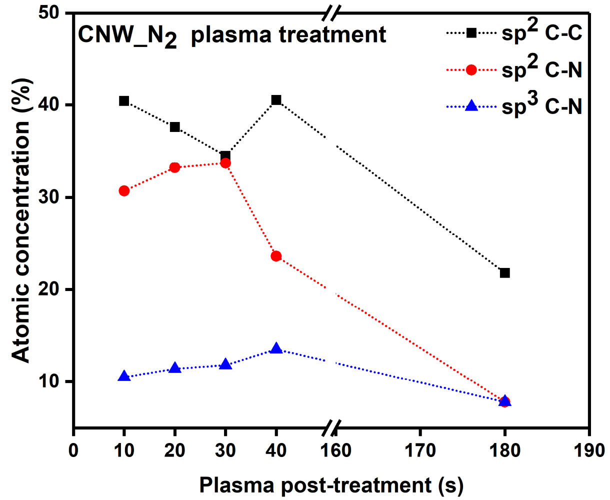
Raman / XPS / NEXAFS

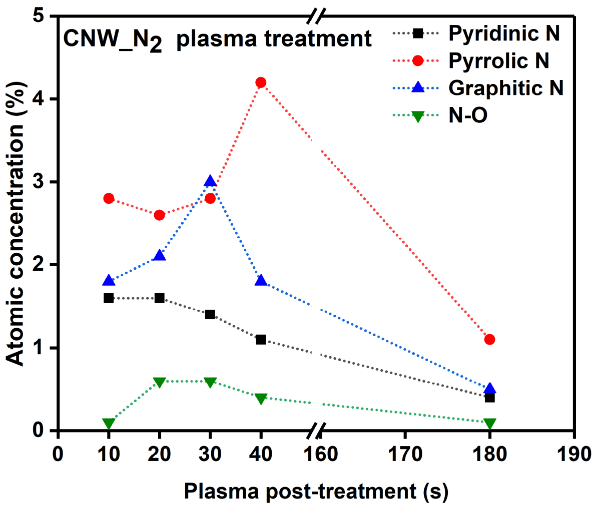
Experimental evidence

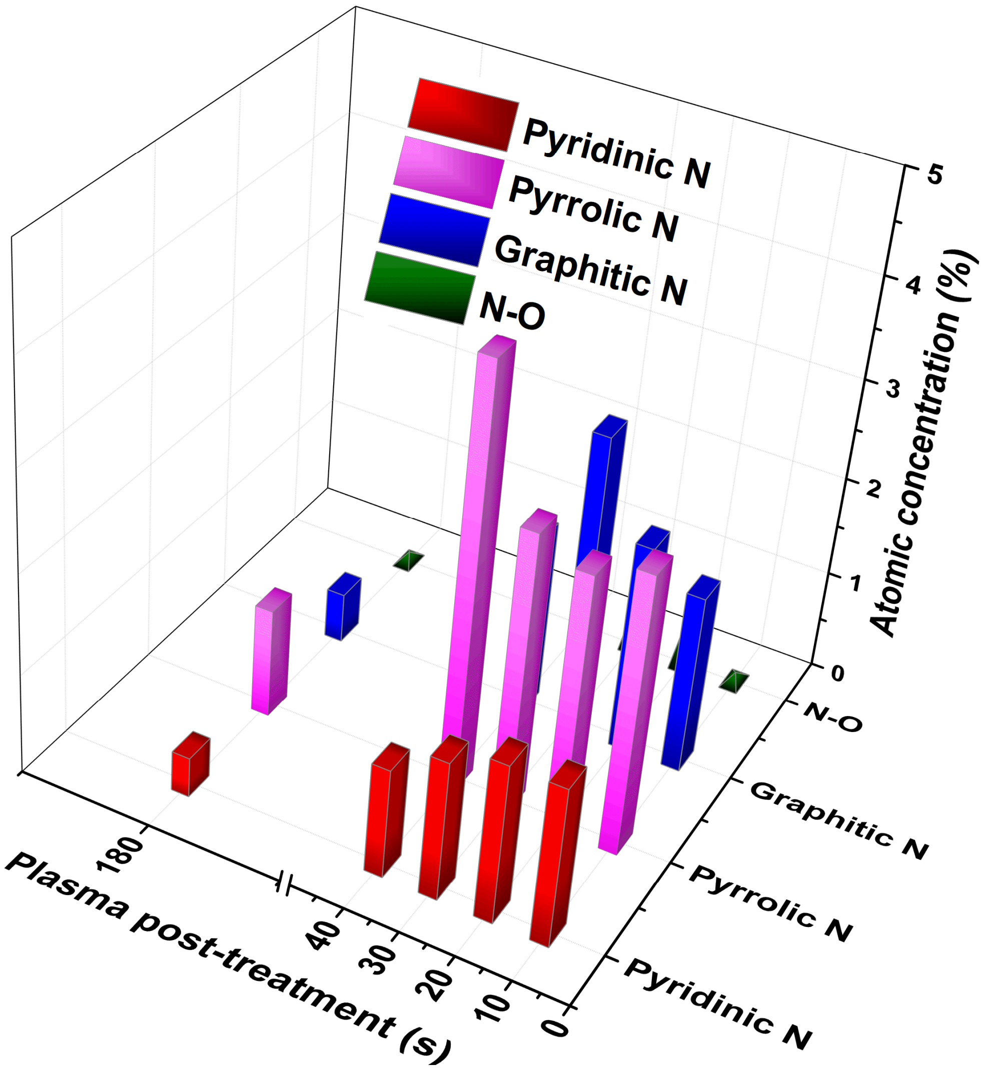
X-ray Photoelectron Spectroscopy Analysis: N 1s Spectra



N-doping results







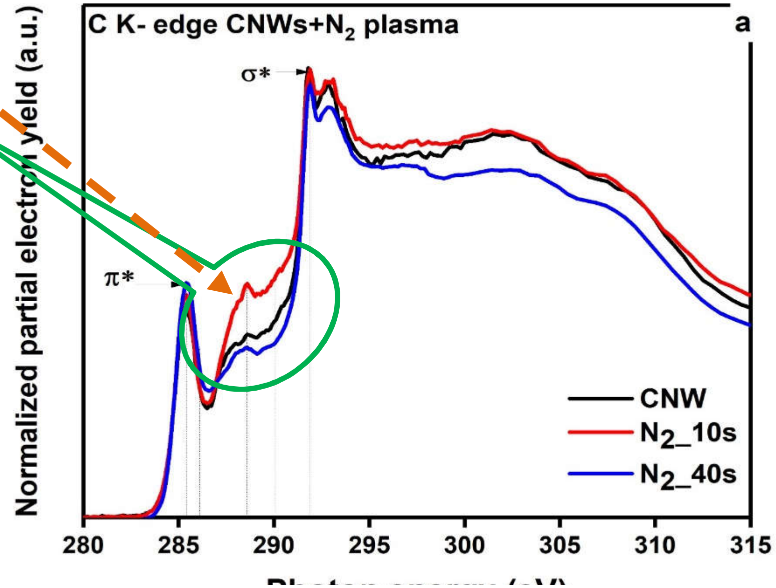
Near Edge X-ray-Absorption Fine-Structure (NEXAFS) Spectroscopy

288.5 eV

"Fingerprint" region

π^* : 285.4 eV

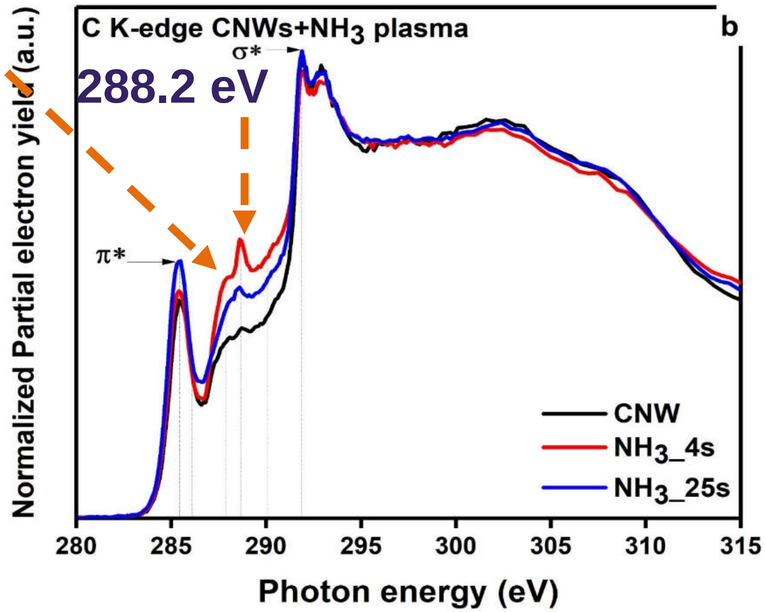
σ^* : 292.0 eV



287.5 eV

π^* : 285.4 eV

σ^* : 292.0 eV



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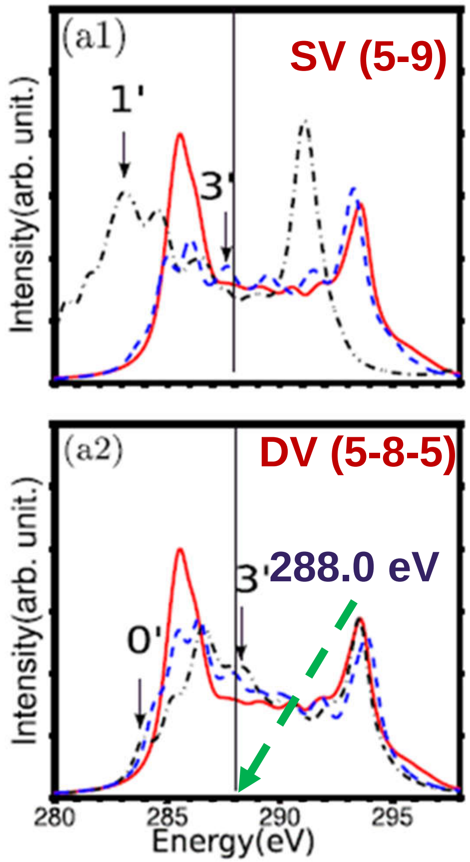
Characteristic Changes After Plasma-treatments

NH_3 Plasma

- Negligible change in the in-plane crystalline size
- In-plane crystalline size lower than the initial value after longer plasma exposure
- Lower concentration of incorporated nitrogen
- Appearance of ‘2 peaks’ in the “fingerprint” region

N_2 Plasma

- *In-plane crystalline size increases with plasma treatment time*
- *Higher concentration of incorporated nitrogen*
- Appearance of ‘1 peak’ in the “fingerprint” region



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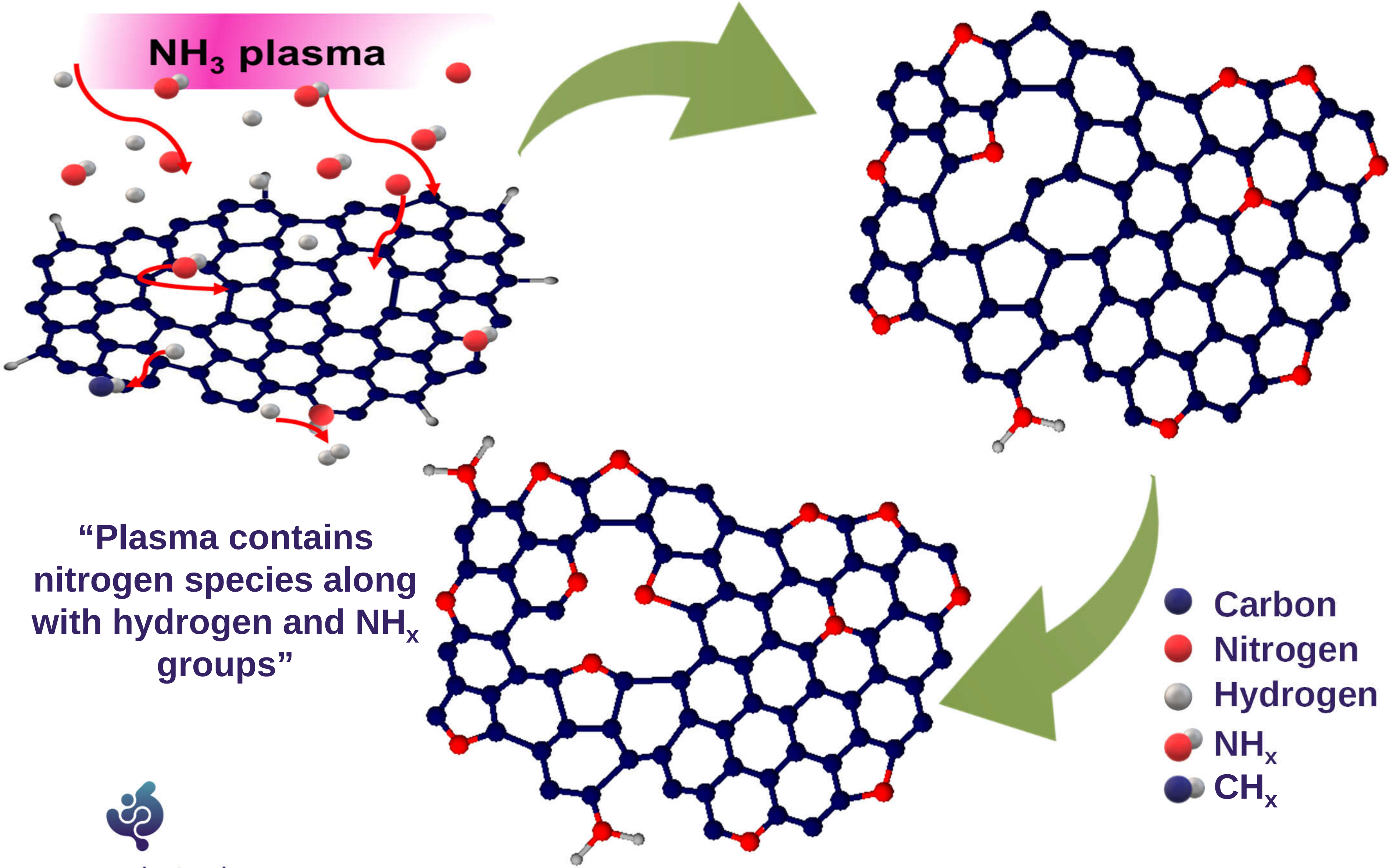
- **Mechanism of Nitrogen Incorporation: NH_3 Plasma**



"Plasma contains nitrogen species along with hydrogen and NH_x groups"

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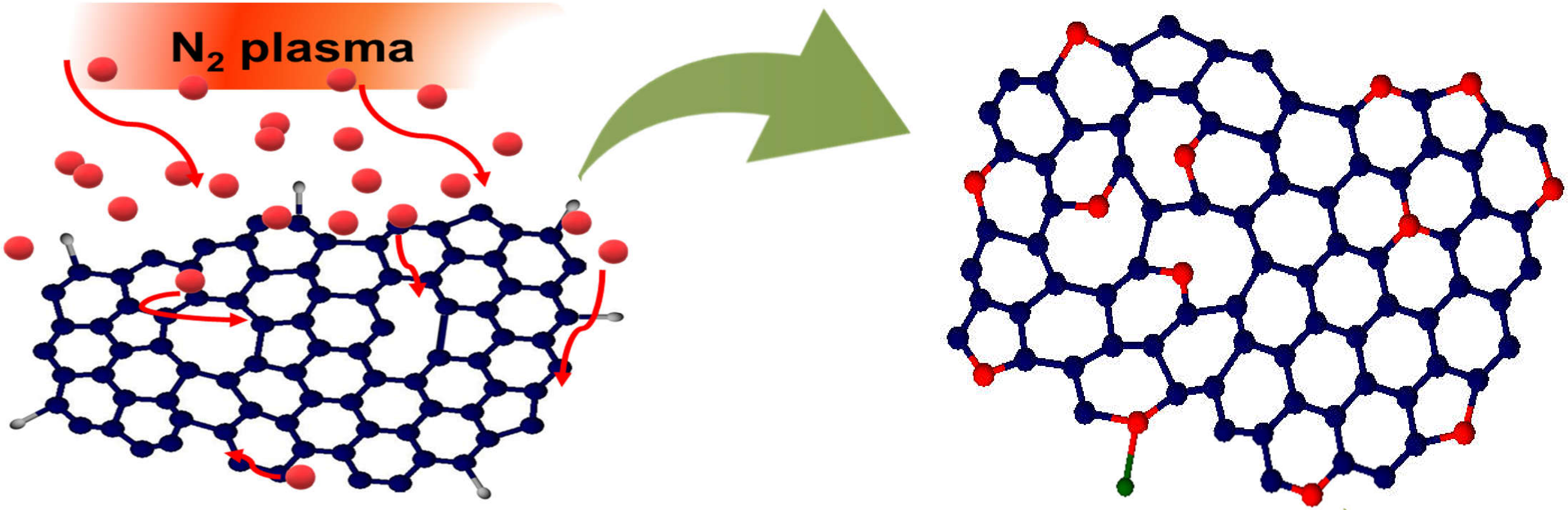
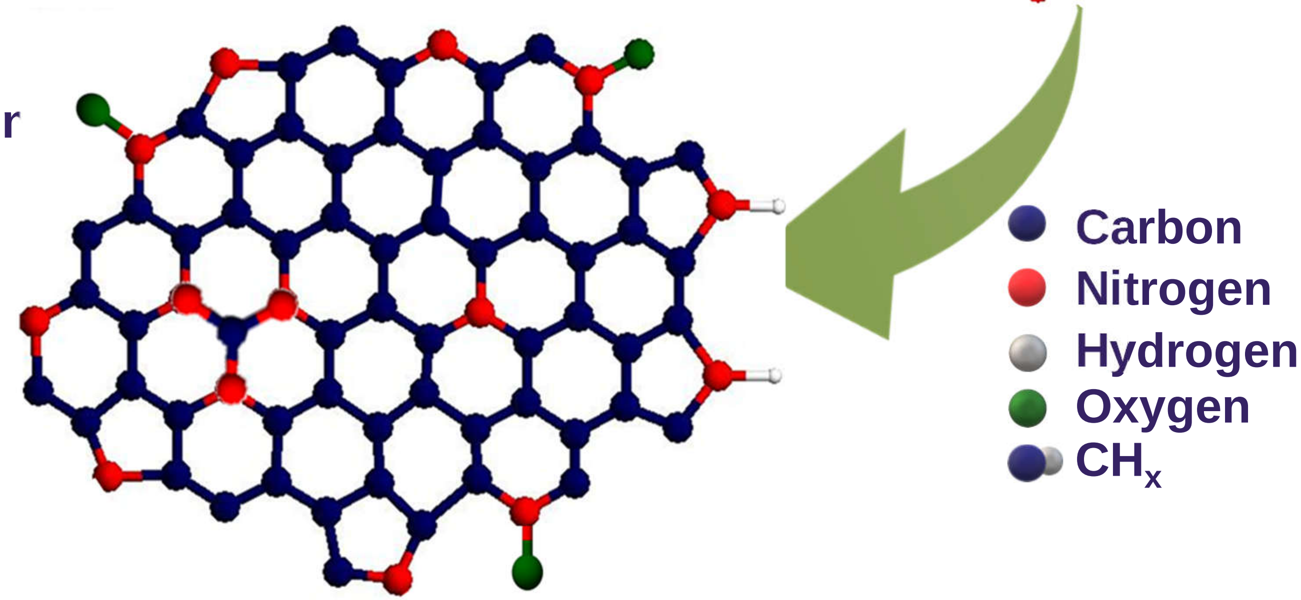
- **Mechanism of Nitrogen Incorporation: N_2 Plasma**



“More excited nitrogen ir plasma”



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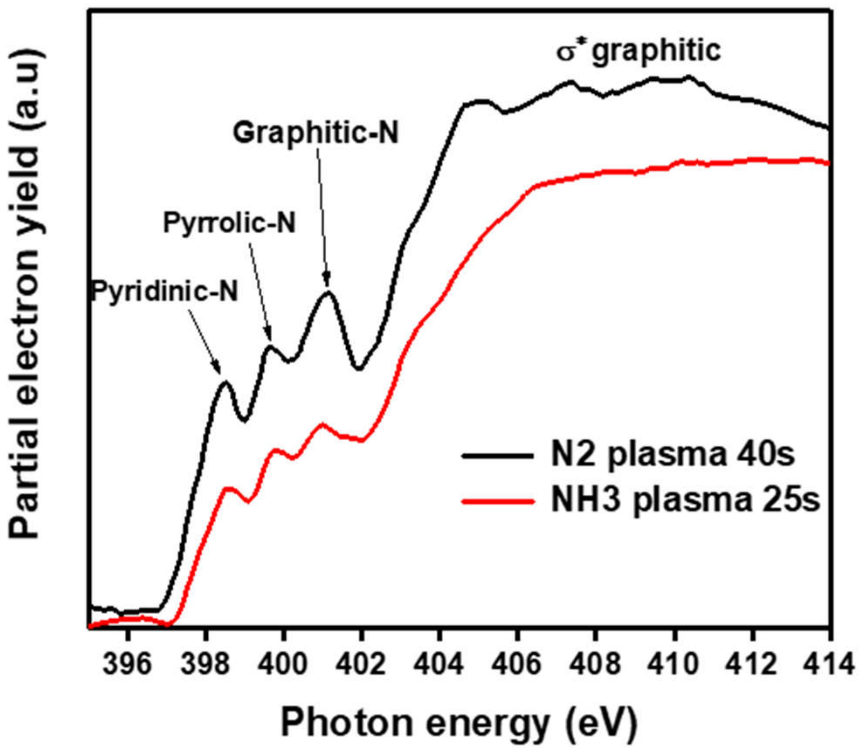
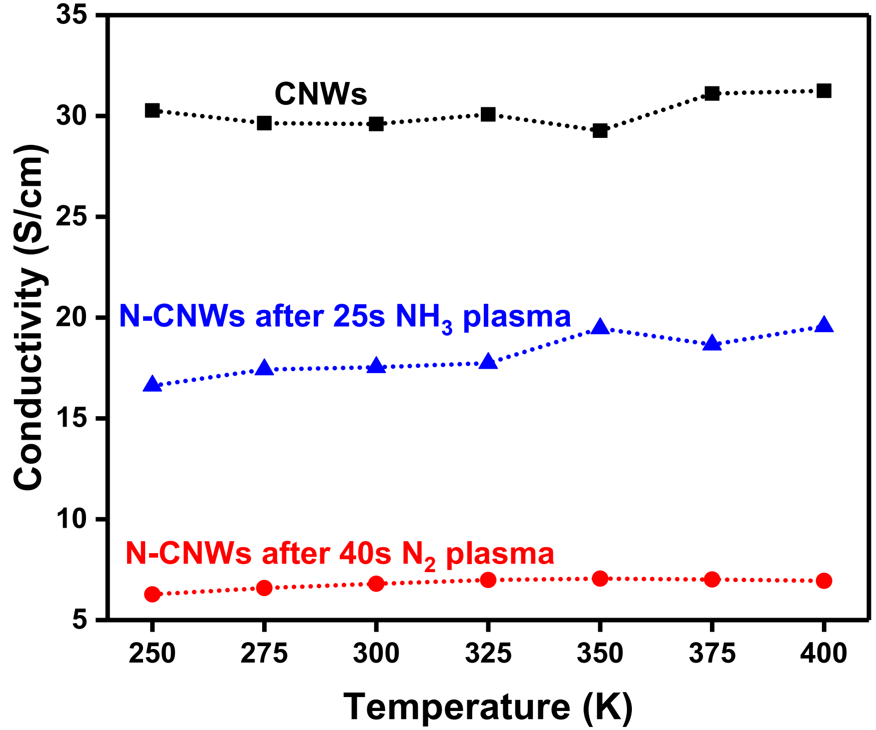
N K edge of N-CNWs



Electrical conductivity



Conclusions

- Plasma design of nanomaterials to replace existing methods, promote large-scale synthesis and advance into applications
- Building of 2D nanostructures with top-down or bottom-up approach using it also to extend to environmental issues
- Advances in developing theoretical models describing and predicting 2D nanoscale growth and synthesis
- Controlling plasma species for building 2D materials
- Extending plasma processing beyond graphene and building 2D materials like N-graphene by proper use of plasmas

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