HOW CAN PLASMAS BUILD CARBON NANOSTRUCTURES?

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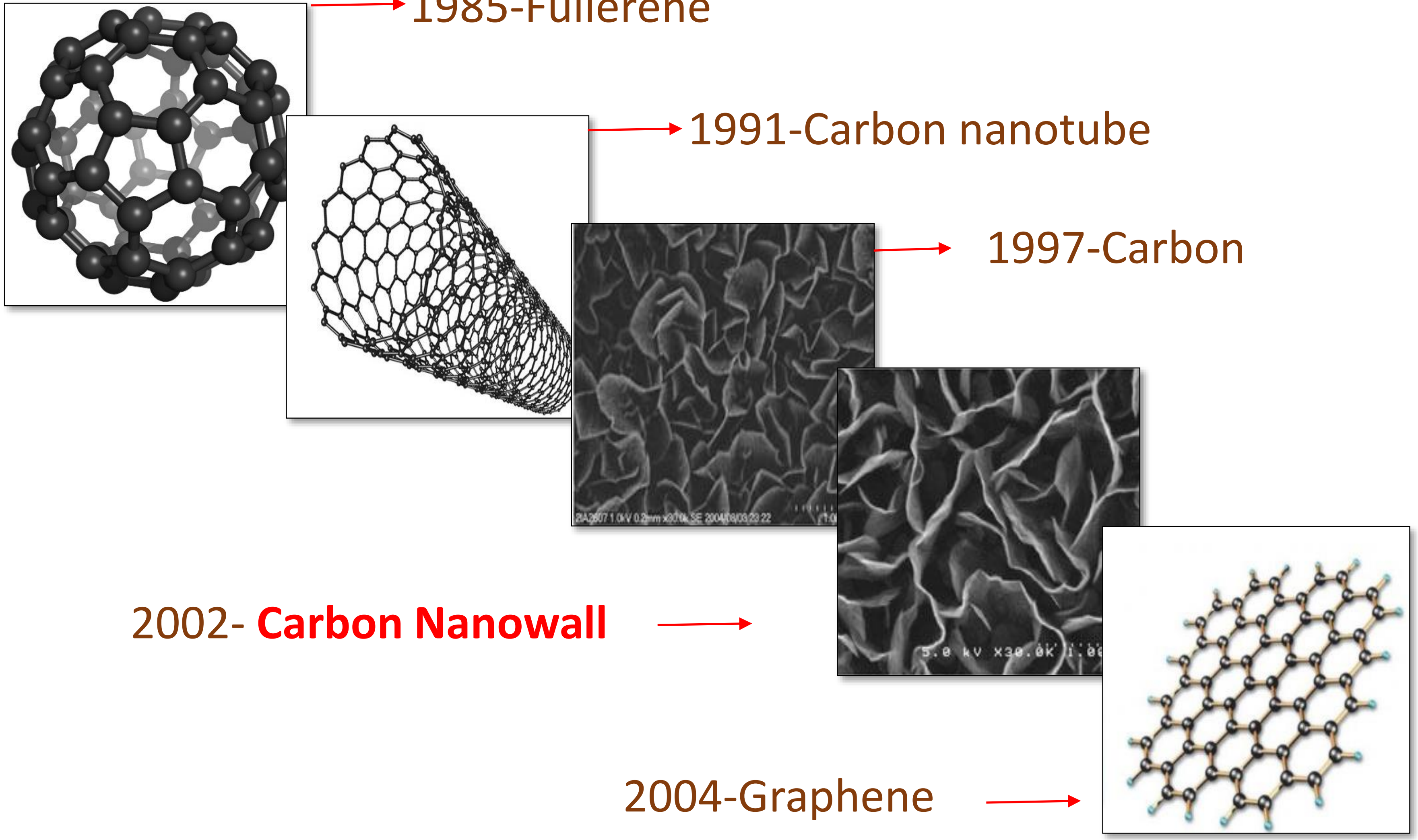
Carbon Nanostructures: Timeline



1985-Fullerene

1991-Carbon nanotube

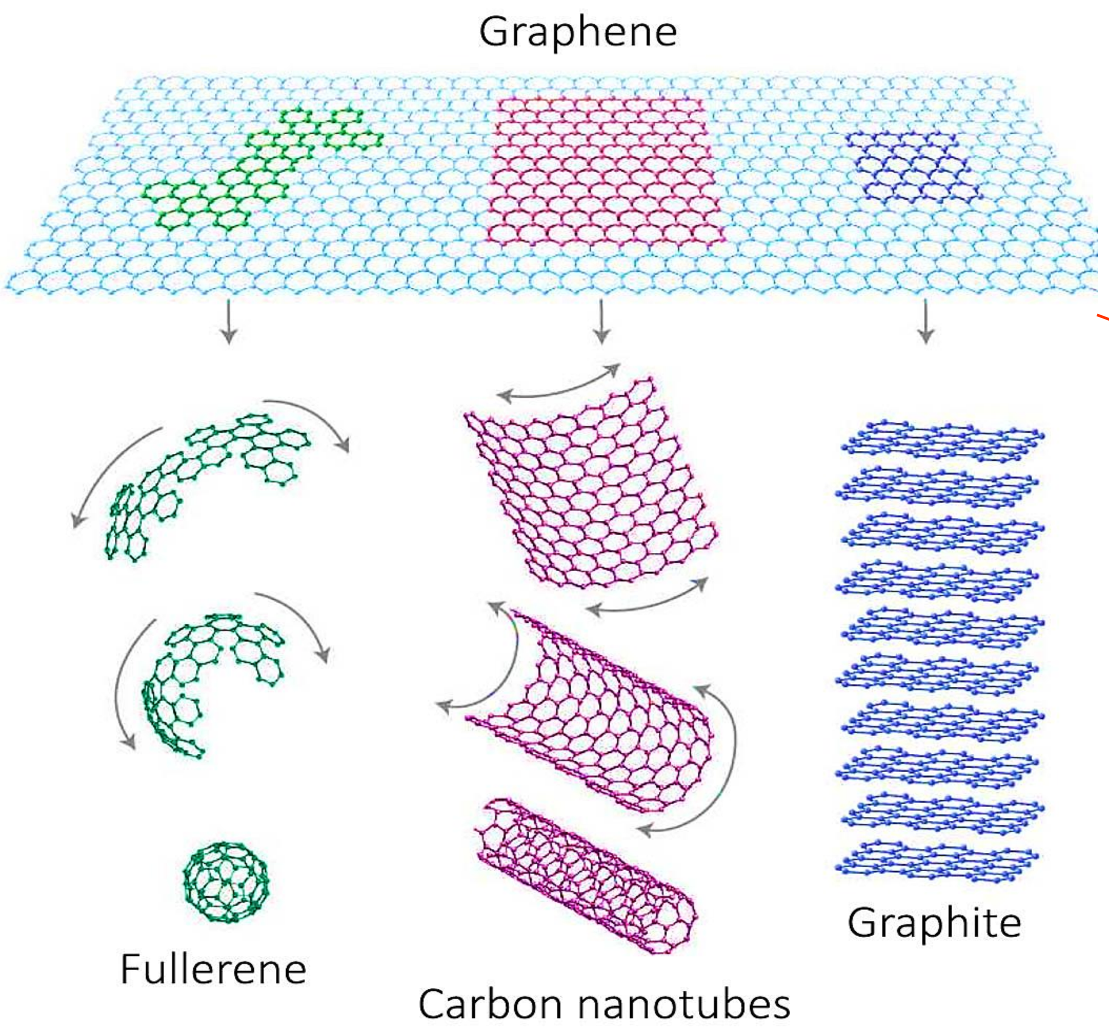
1997-Carbon

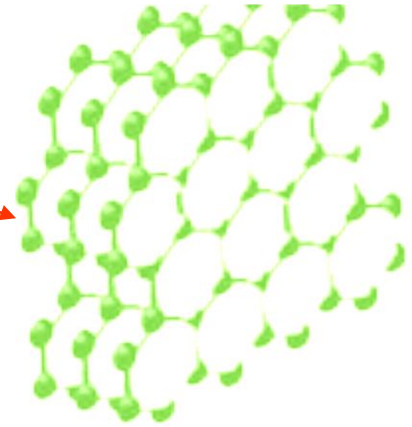
2002- **Carbon Nanowall**

2004-Graphene

1. Ando, Y.; Zhao, X.; Ohkohchi, M. *Carbon N. Y.* **1997**, *35*, 153–158, doi:10.1016/S0008-6223(96)00139-X.
2. Wu, Y.; Qiao, P.; Chong, T.; Shen, Z. *Adv. Mater.* **2002**, *14*, 64–67, doi:10.1002/1521-4095(20020104)14:1<64::AID-ADMA64>3.0.CO;2-G.

Graphene : Constituent of Carbon Nanostructures

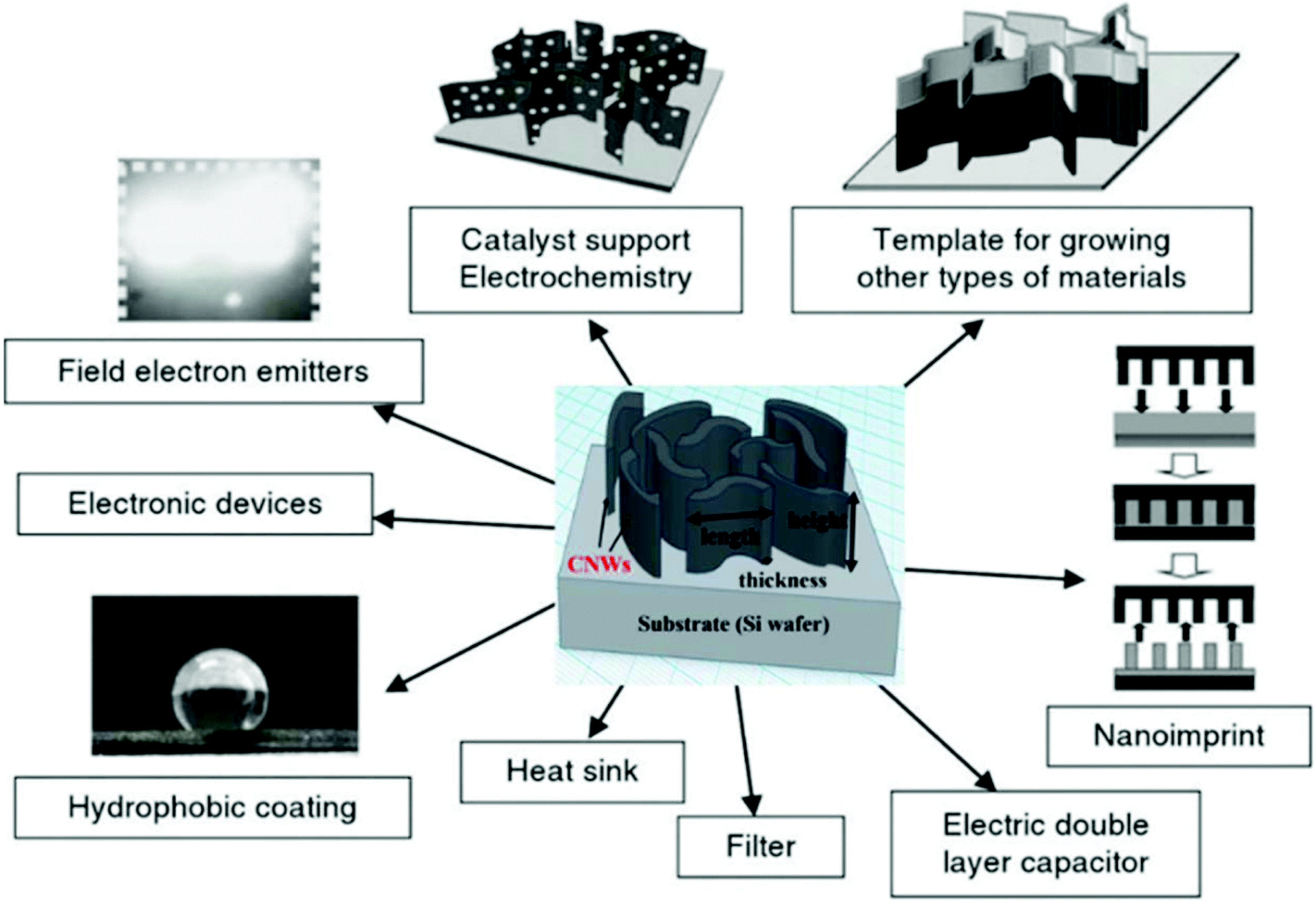




Carbon Nanowalls (CNWs) or
Graphene nanowalls (GNWs)
Vertically aligned 2D
carbon nanosheets

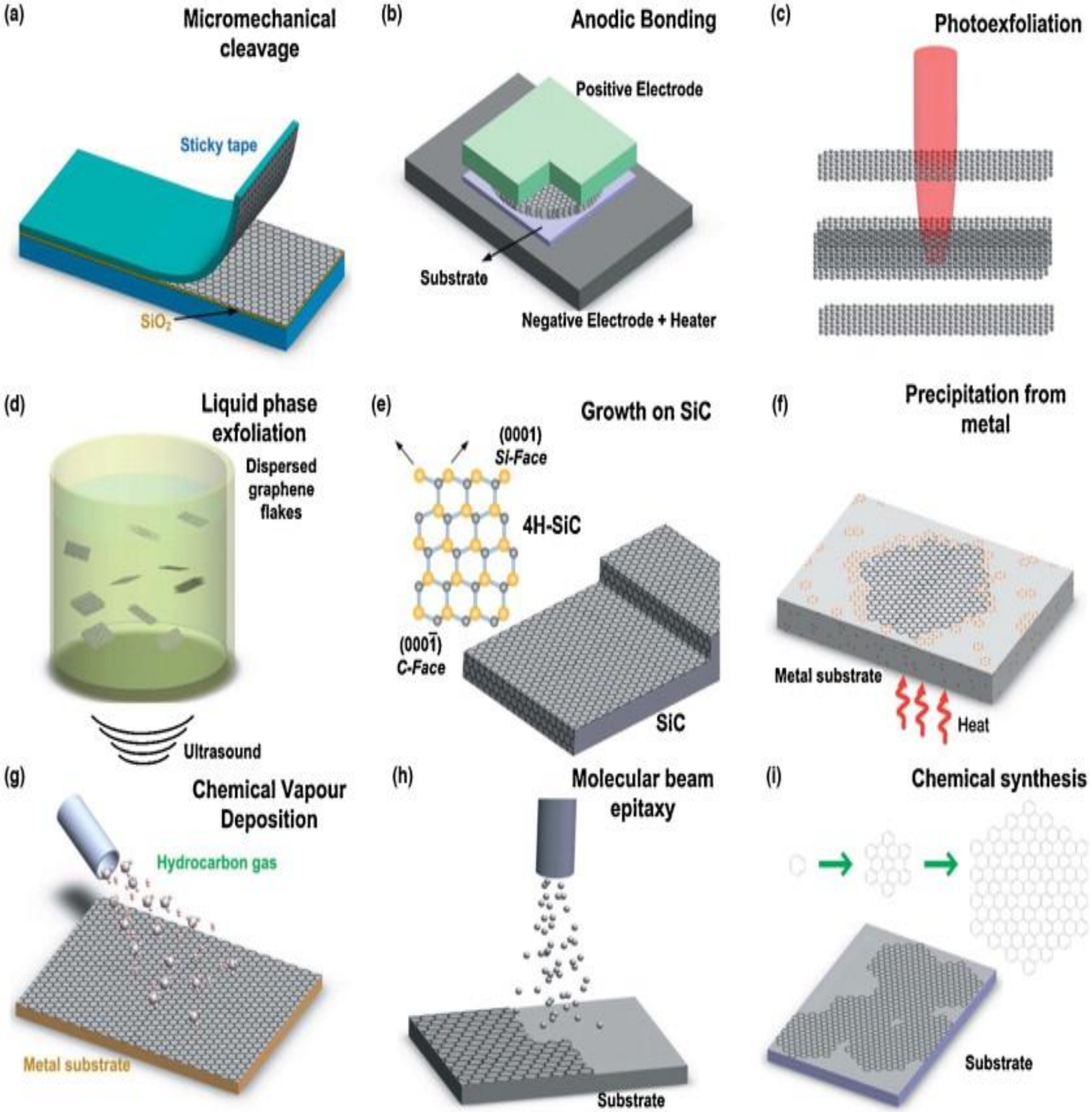
M. Hiramatsu and M. Hori, in *Carbon Nanowalls: Synthesis and Emerging Applications*, Springer, Vienna, 2010, ch. 1, p. 5

Why Carbon Nanowalls…?

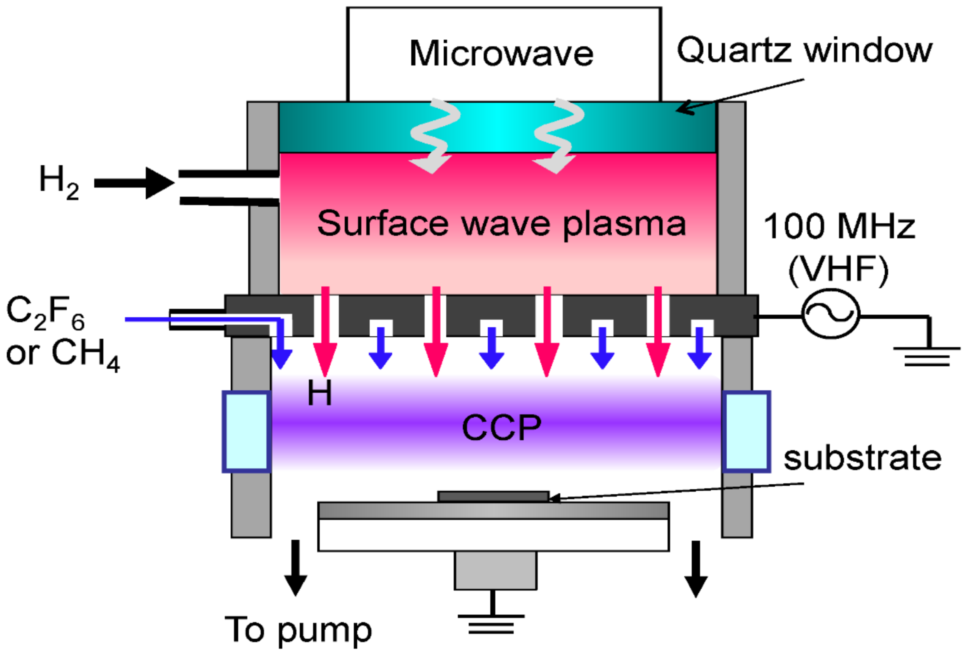


M. Hiramatsu and M. Hori, in *Carbon Nanowalls: Synthesis and Emerging Applications*, Springer, Vienna, 2010, ch. 1, p. 5

Why Plasma-processing Techniques..?



Plasma assisted method

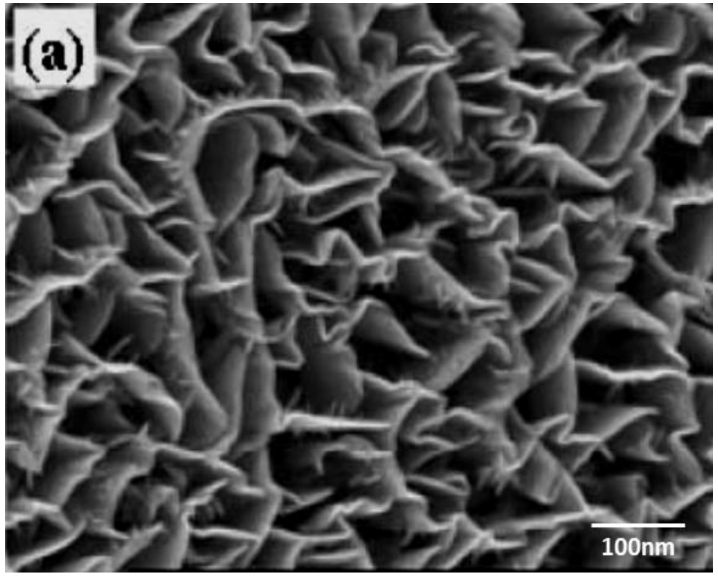


- ❖ *Large scale growth with selected properties*
- ❖ *Control in ordering/patterning*
- ❖ *Rapid production and fast processing*
- ❖ *Easier and safer*

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

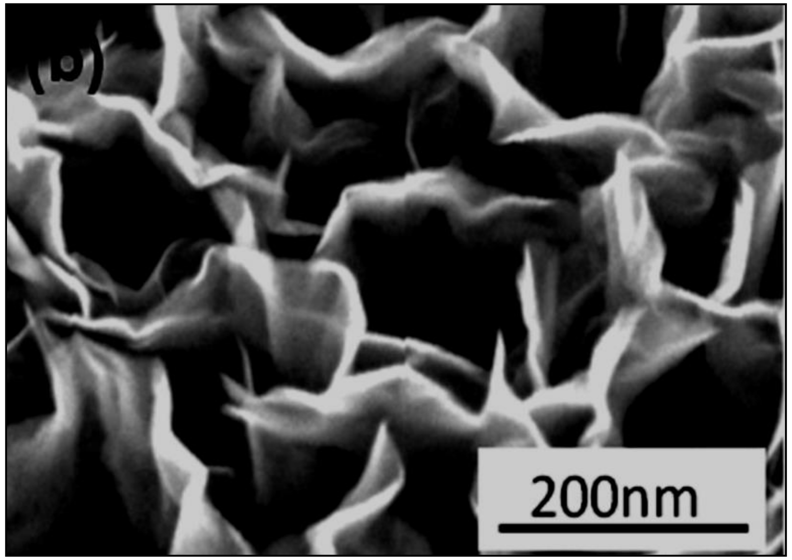
Plasma-assisted Synthesis Methods

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



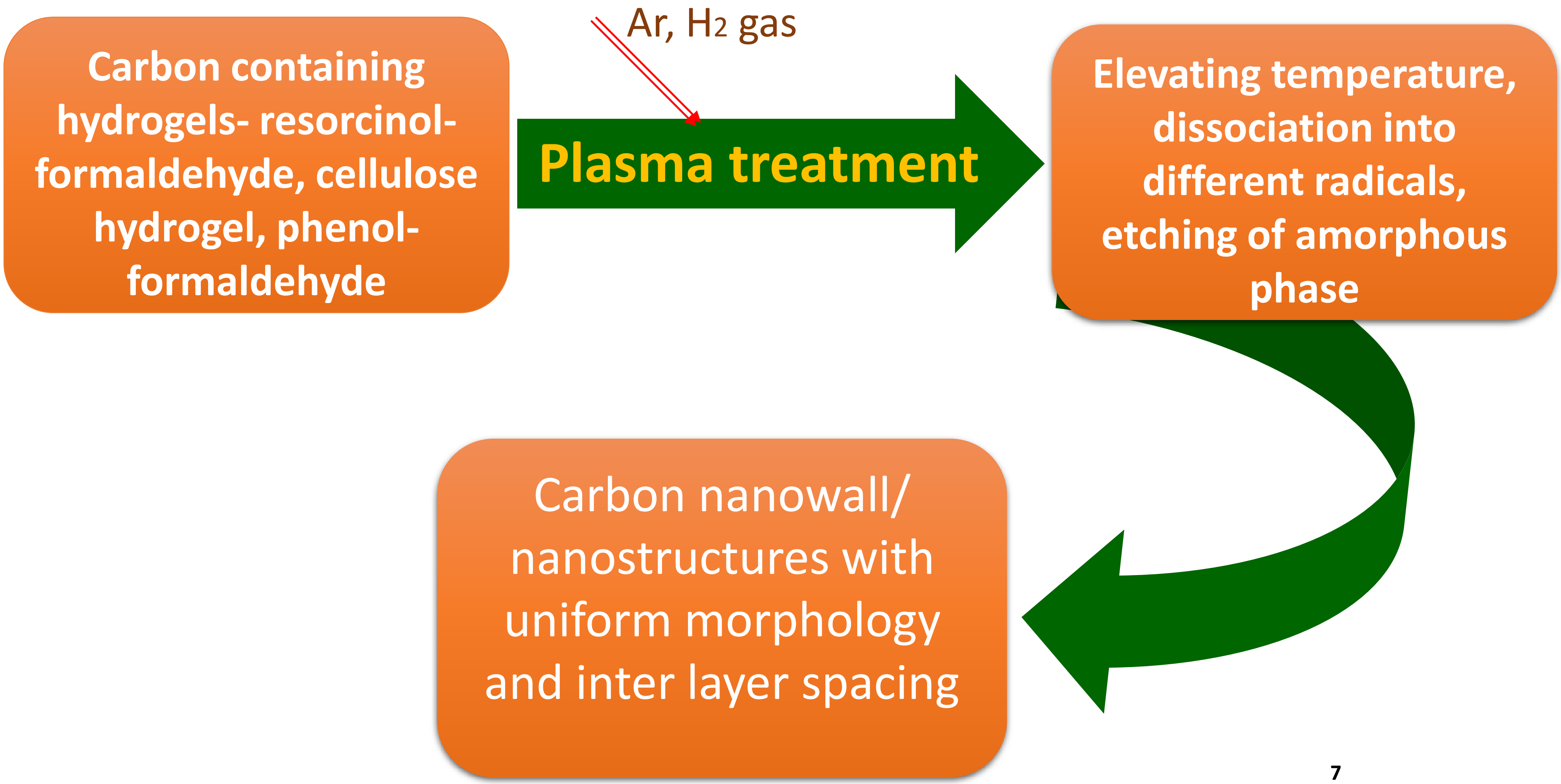
Wu, Y.; Yang, B.; Zong, B.; Sun, H.; Shen, Z.; Feng, Y. J. Mater. Chem. ***2004****, 14*

- ***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*

Plasma Treatment On Solid/Liquid Carbon Sources



Carbon containing hydrogels- resorcinol-formaldehyde, cellulose hydrogel, phenol-formaldehyde

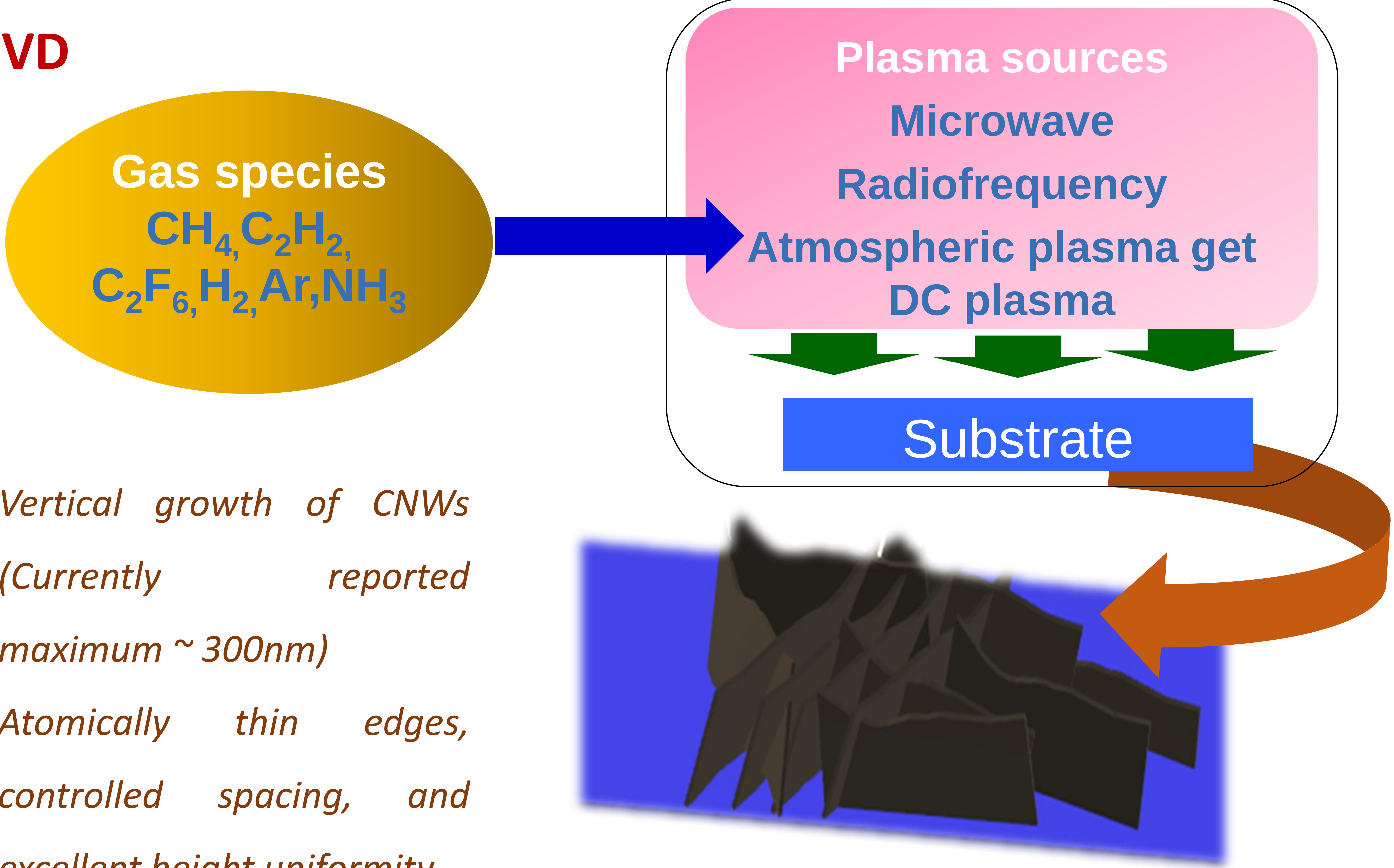
Ar, H_2 gas

Plasma treatment

Elevating temperature, dissociation into different radicals, etching of amorphous phase

Carbon nanowall/ nanostructures with uniform morphology and inter layer spacing

PECVD



Gas species

$CH_4, C_2H_2, C_2F_6, H_2, Ar, NH_3$

Plasma sources

Microwave

Radiofrequency

Atmospheric plasma get

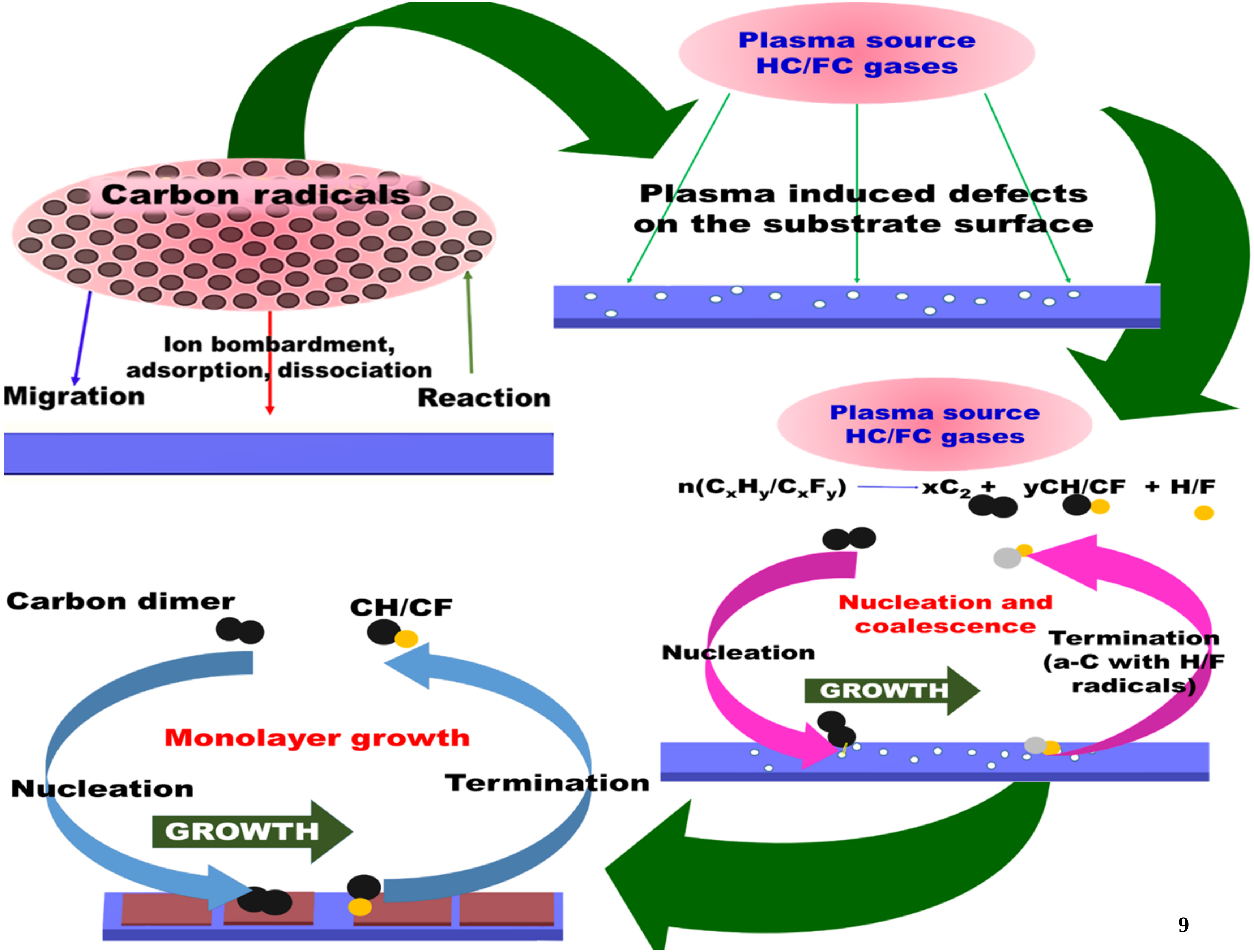
DC plasma

Substrate

Carbon nanowall

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

Plasma Enhanced Growth of CNWs - Mechanism

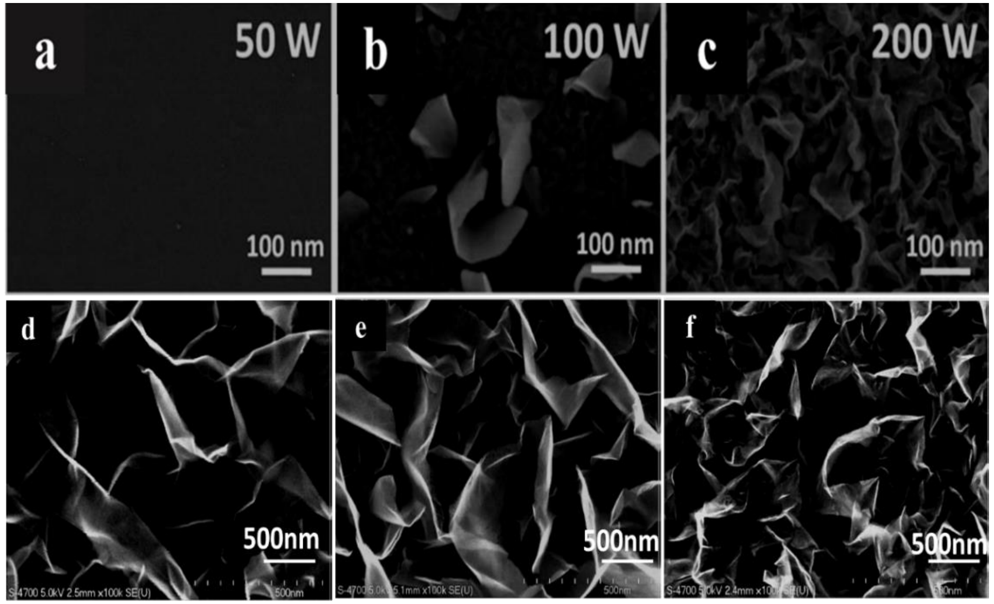


Discharge Parameters

Finding optimum discharge parameters for the high yield growth

Different plasma power

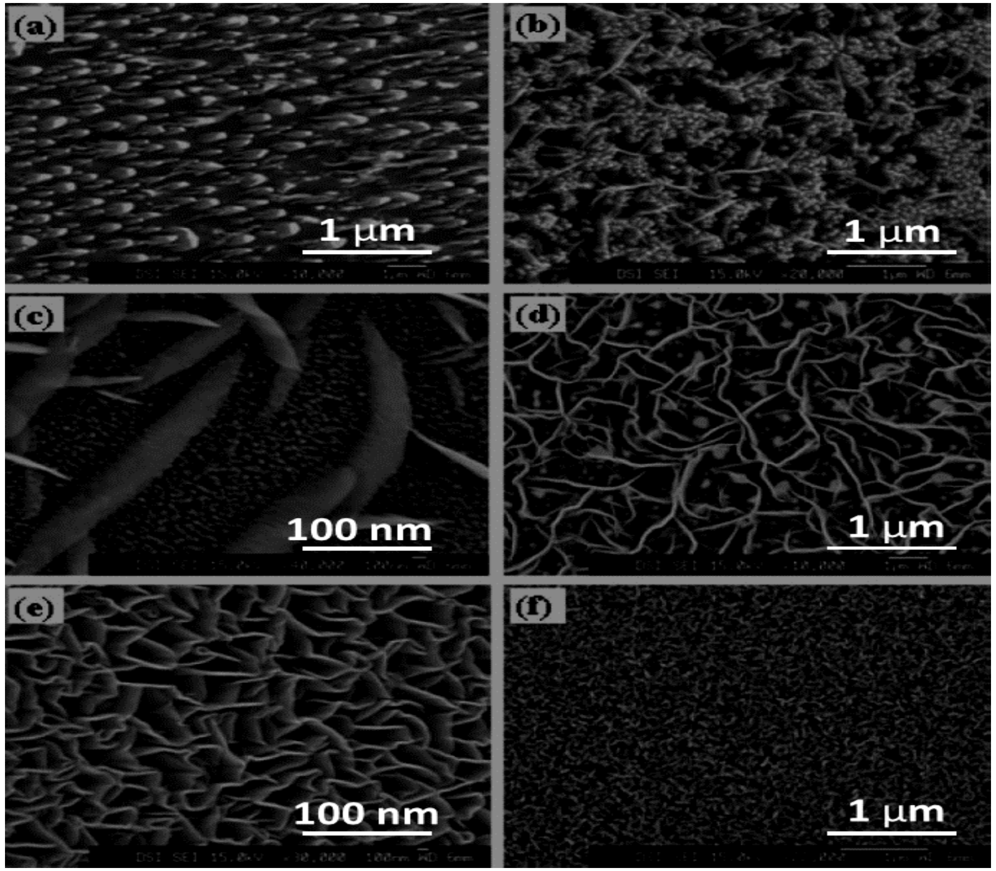
*Yang, C.; Bi, H.; Wan, D.; Huang, F.; Xie, X.; Jiang, M. Direct J. Mater. Chem. A **2013**, 1, 770–775,*



CH_4 concentration

d) 10%, e) 40%, f) 100%

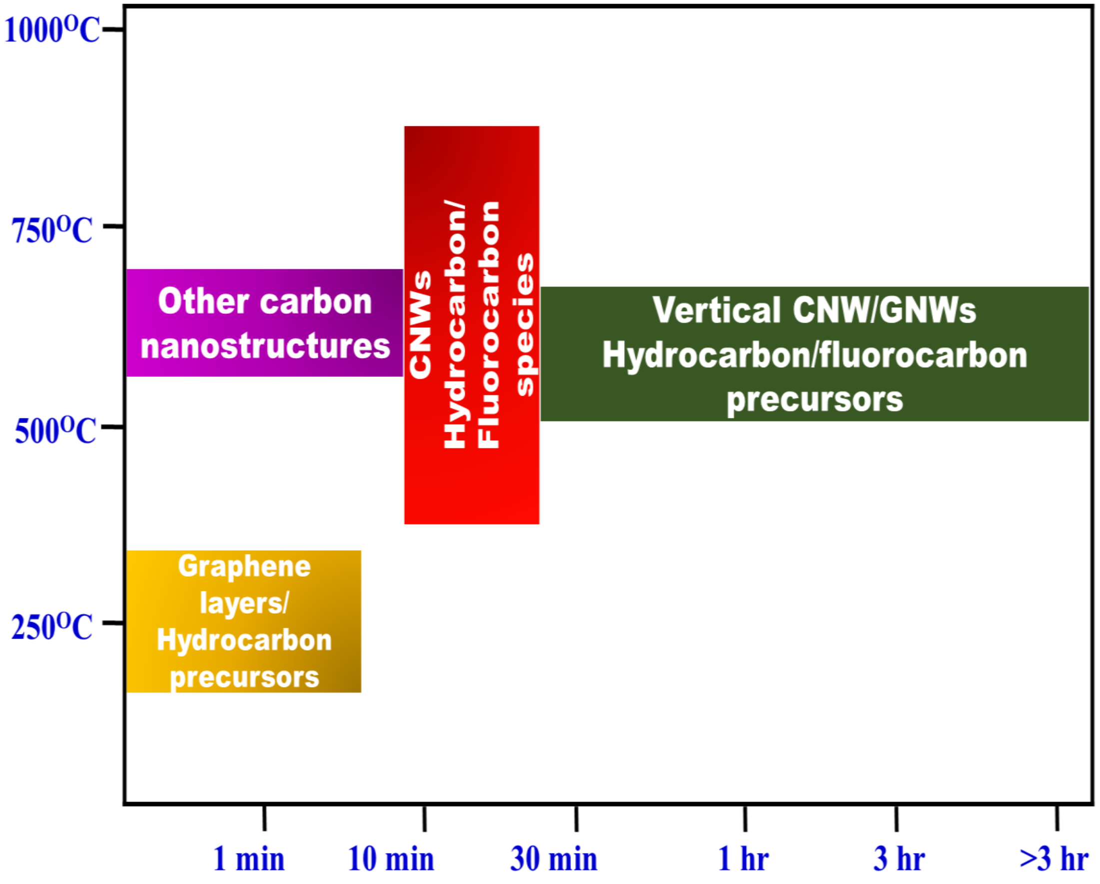
*Wang, J.; Zhu, M.; Outlaw, R. A.; Zhao, X.; Manos, D. M.; Holloway, B. C., Carbon N. Y. **2004**, 42, 2867–2872,.*



Different H_2/CH_4 flow rate ratios: (a) 30, (b) 15, (c) 10, (d) 6, (e) 4, (f) 1sccm

*Wu, Y.; Yang, B.; Zong, B.; Sun, H.; Shen, Z.; Feng, Y. J. Mater. Chem. **2004**, 14, 469,*

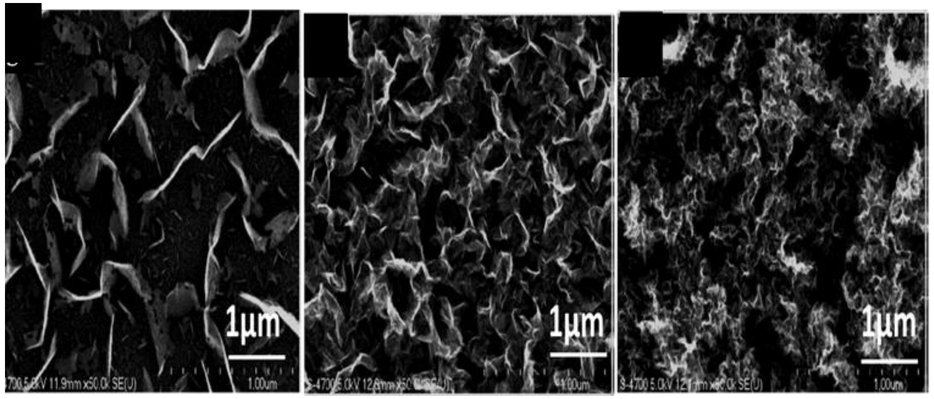
Substrate Temperature and Growth Time



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

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,.*

Enhance the thermal stability of CNWs

Effect of Pressure

Lower plasma pressure

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

Higher plasma pressure

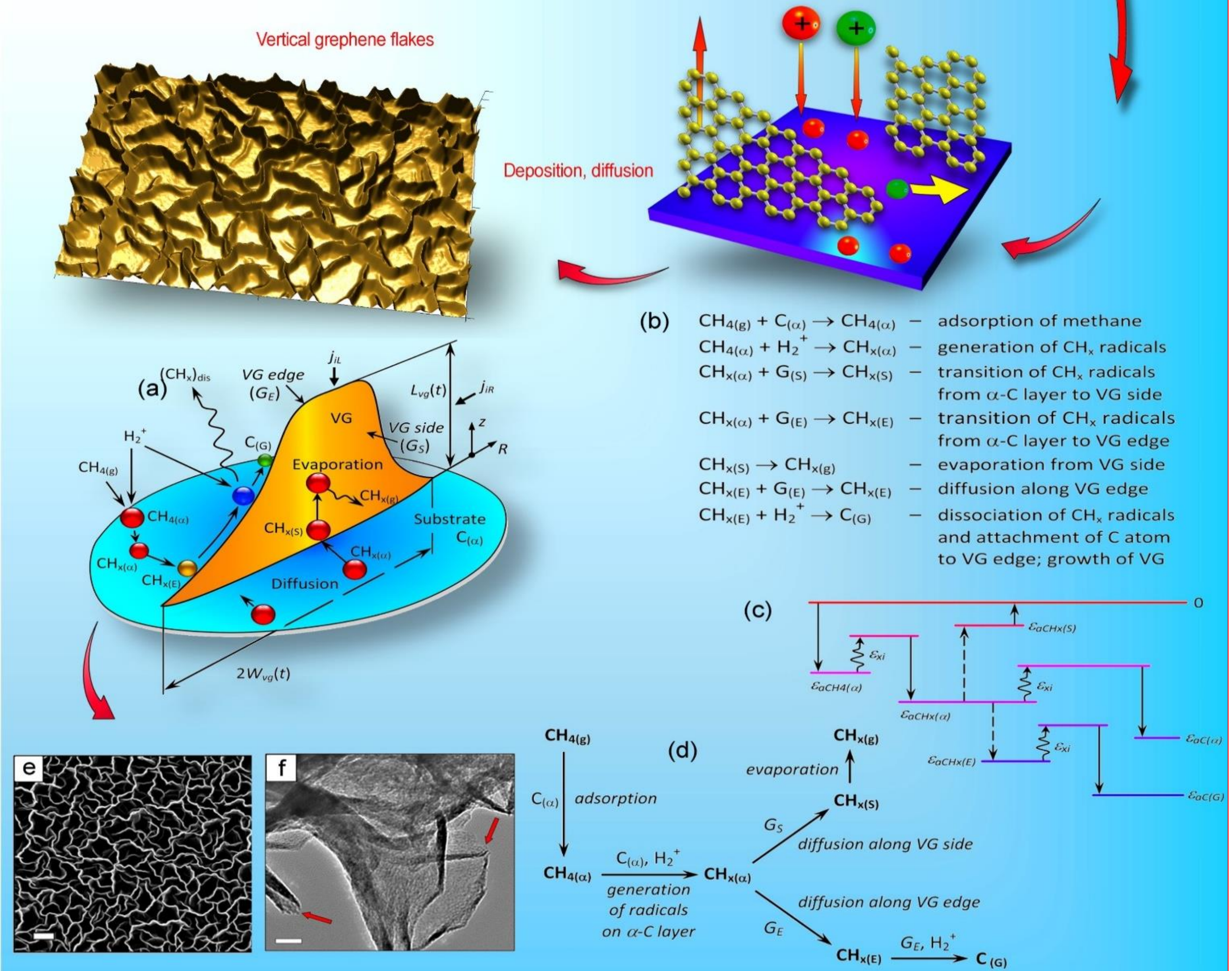
- ✓ Larger volume of feedstock gas input
- ✓ Electron energy decreased
- ✓ The massive production

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

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.*



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.

The ion bombardment changes the adsorption mechanism on the substrate where the methane molecules (primary source of CHx radicals) adsorb, from the physical sorption (~ 0.5 eV) to the chemical sorption (~ 1-2 eV), to generate the large amount of the radicals on the surface at the elevated temperatures. The radical can diffuse[i],[ii] along the surface layer, and can be adsorbed on the GNF flat side or sharp edge during the diffusion, at that the adsorption energy is changed from $\varepsilon_a CH_X(\alpha)$ to $\varepsilon_a CH_X(S)$ or $\varepsilon_a CH_X(E)$, respectively. If the radical is adsorbed on the high-defect GNF edge, the adsorption energy is increased:

$(\varepsilon_a CH_X(\alpha) \rightarrow \varepsilon_a CH_X(E))$,

and the radical can diffuse along the edge with low probability of evaporation or transition to the side surface of the GNF sheet $(\varepsilon_a CH_X(G) >> \varepsilon_a CH_X(S))$, see Fig. 1.

Furthermore, the model implicates several features:

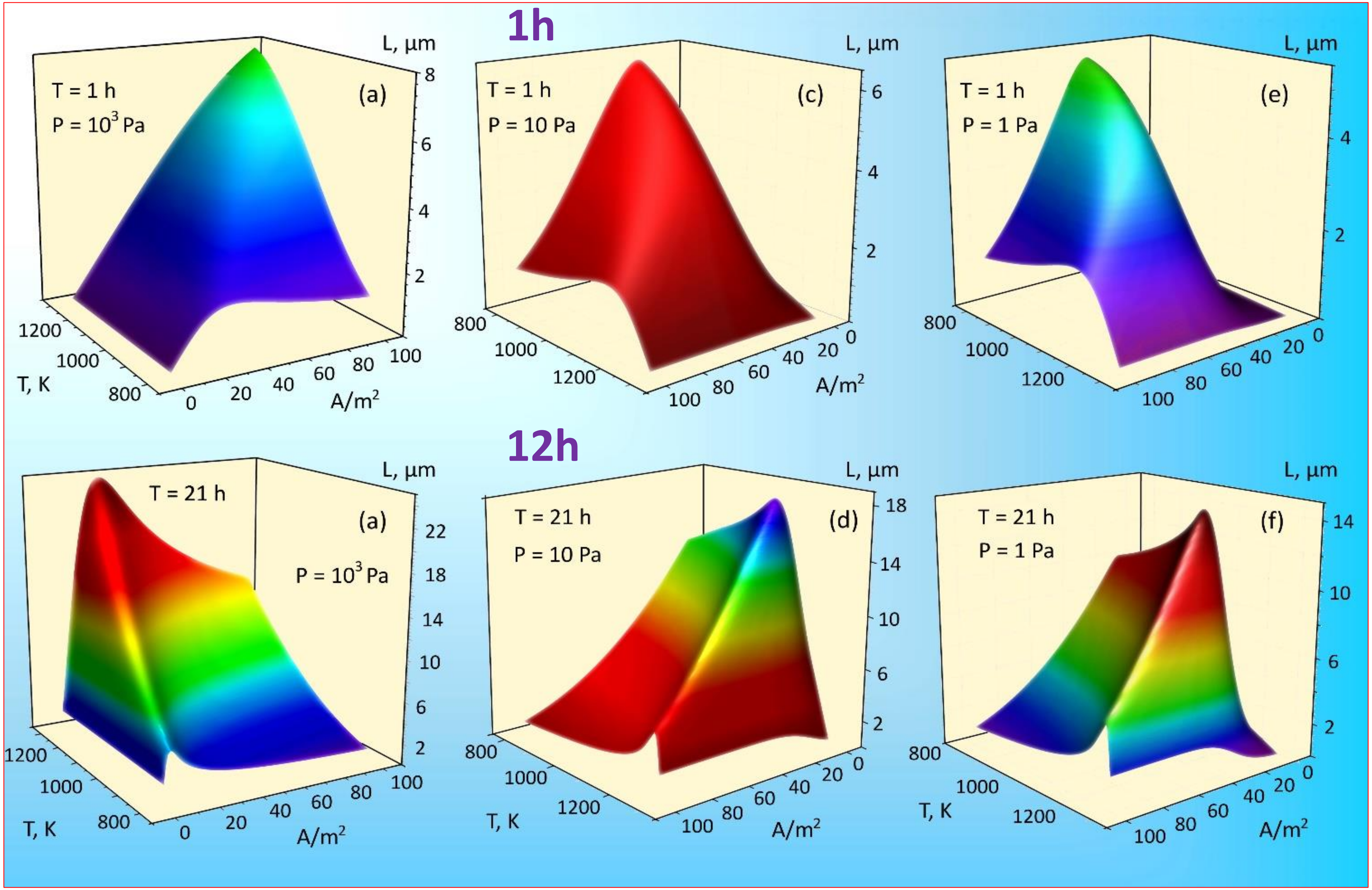
(i) The **nanoflakes morphology was explained by the difference between the energy** of the physical sorption $\varepsilon_a CH_X(S)$ on the defect-free flat surface of nanoflake, and the energy $\varepsilon_a CH_X(E)$ of the chemical sorption on the defected edges of the GNF. The GNF grow when CH_X radical is struck by ion at the diffusion from the GNF bottom to the top, and the carbon atom is released.

(ii) (As suggested by a number of researchers,[14,29] **the electric field on the exposed sharp edges of the nanoflakes is taken into account** when describing the GNF growth. Strong enhancement of the electric field by sharp edges of a nanoflake plays a vital role in the GNF growth, since it intensifies the reactions by order of a magnitude at the ion focusing.

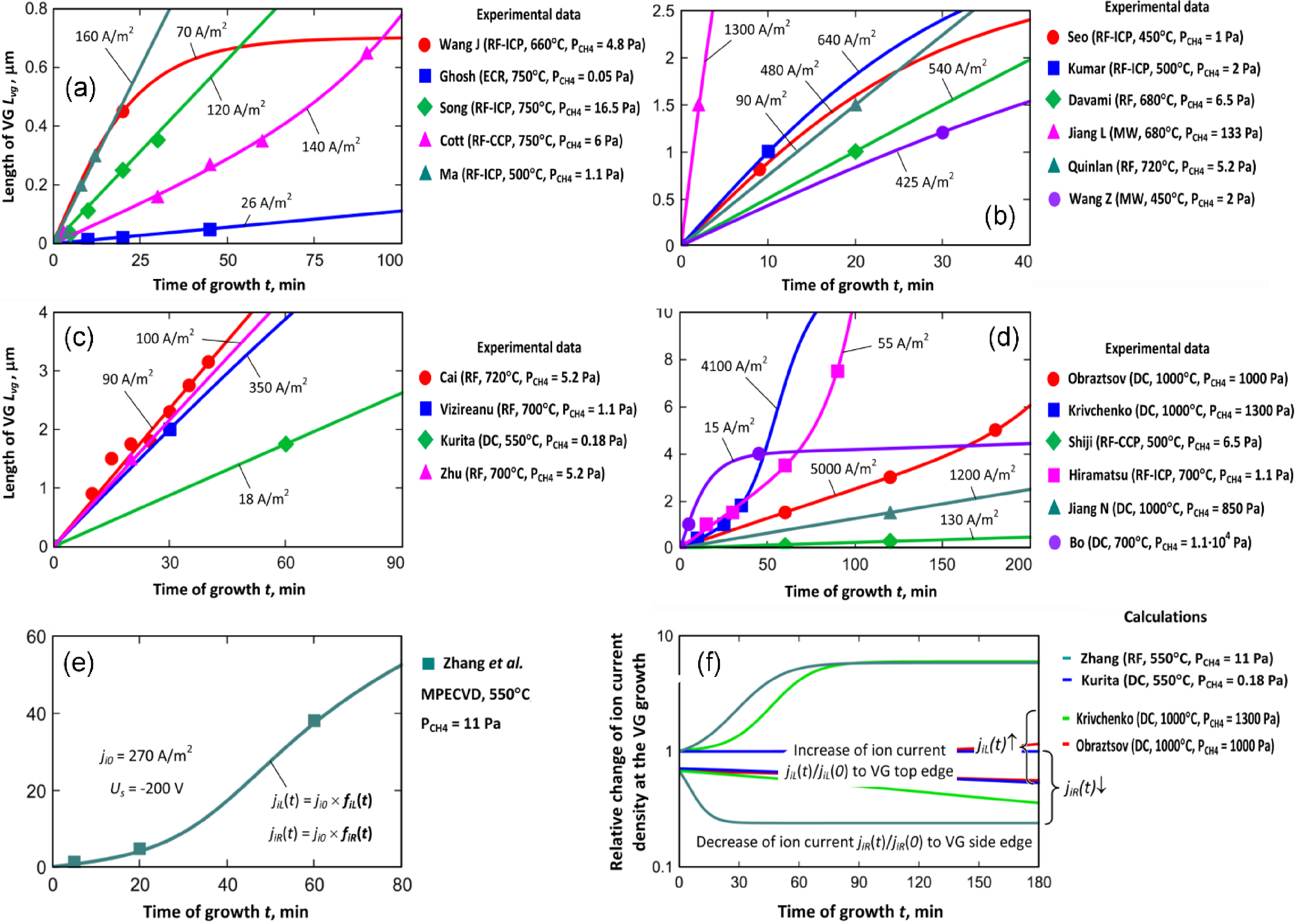
(iii) The **diffusion of radicals from the substrate to the GNF top** and the growth of the GNF in width depend on the ion current density j_{iR} to the side, while the nanoflake growth in height depends on the ion current density j_{iR} to the top; a re-distribution of the densities occurs at the nanoflakes growth.

(iv) **The current densities to the side and top edges** of the nanoflake change during the growth because of shielding of the nanoflakes side edge by the neighboring nanoflakes after the GNF array grows high.

Nanoflake length

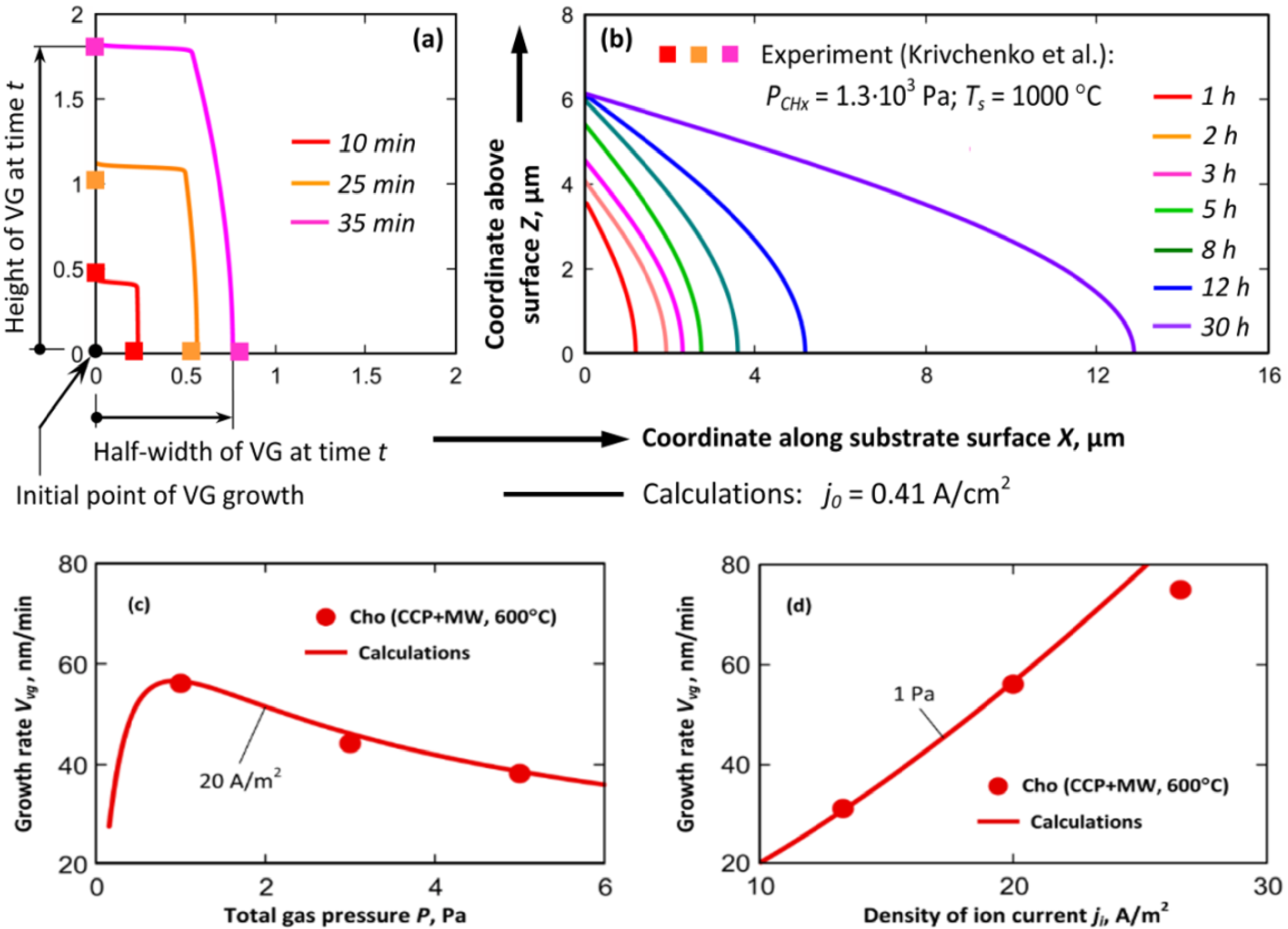


Big data”, i.e. large volume of information obtained from the multiscale multifactor model allows comprehensive analyzation of the graphene formation and growth as a function of all essential parameters and processes in plasma.



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.

On the experimental side …

CH-CNWs Experimental

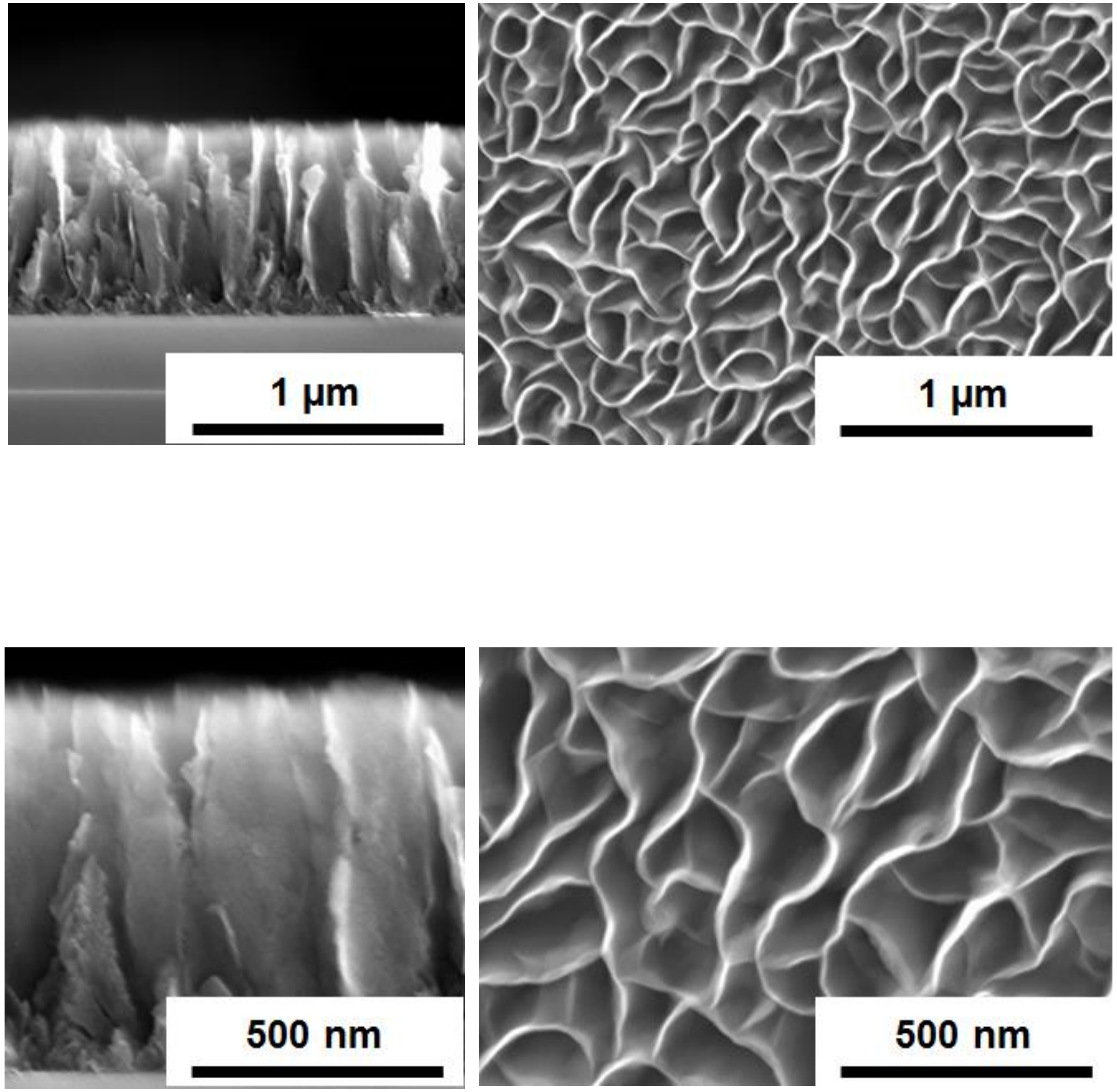
CF-CNWs Experimental

RI-PECVD system
(Radical Injection Plasma Enhanced CVD)

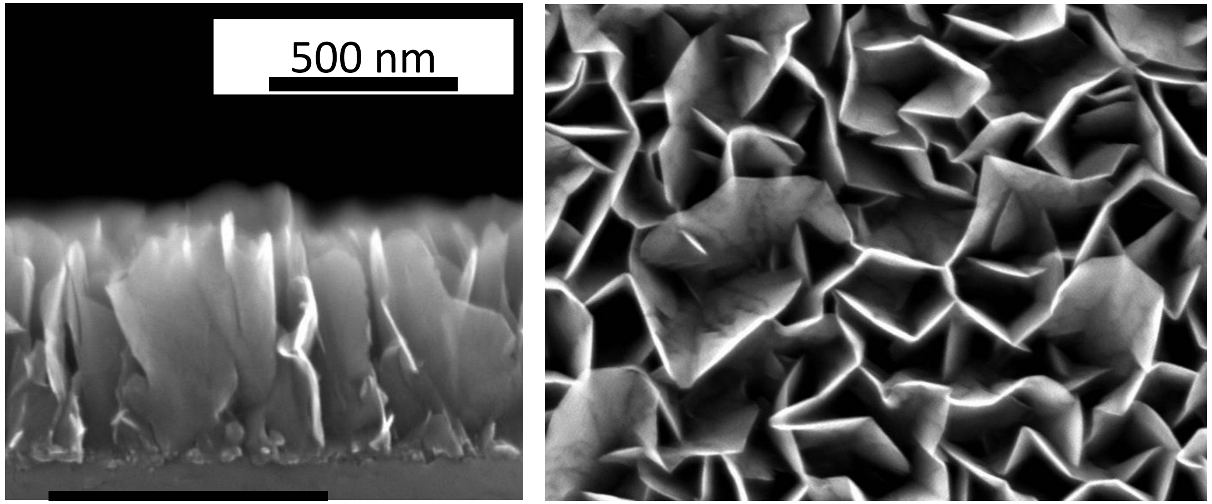
- ✓ CH_4 : 100 sccm H_2 : 50 sccm
- ✓ Substrate : SiO_2
- ✓ Working pressure : 1 Pa
- ✓ Temperature : 600°C
- ✓ SWP power : 400 W
- ✓ CCP power : 300 W

Gas flow rates
H_2 : 100 sccm C_2F_6 : 50 sccm
Pressure : 133 Pa
Substrate temperature : 630˚C
Microwave power : 250 W
VHF power : 250 W
Growth time : 40 min

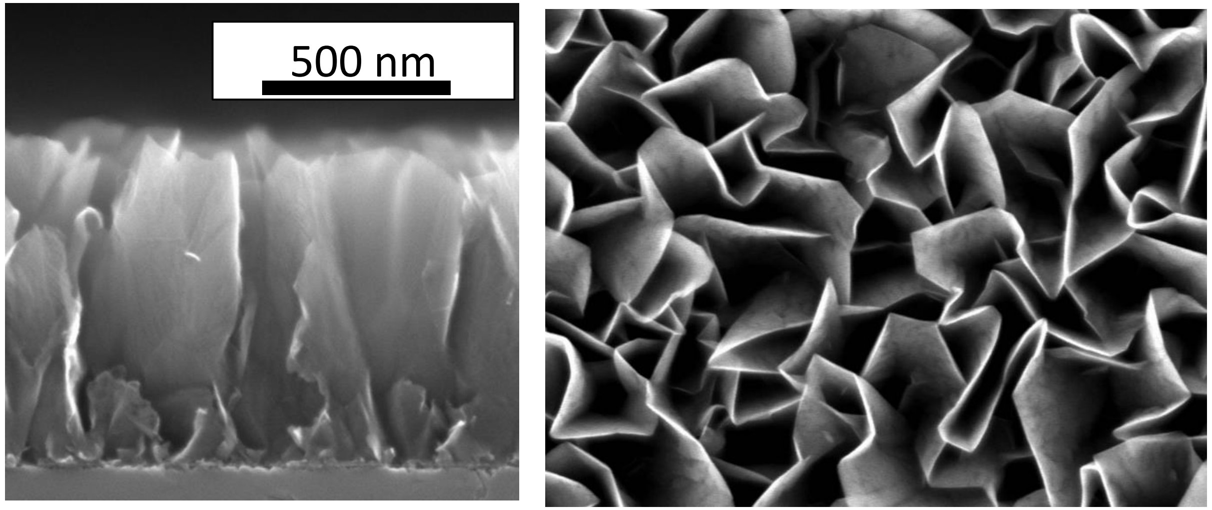
CH-CNWs SEM images



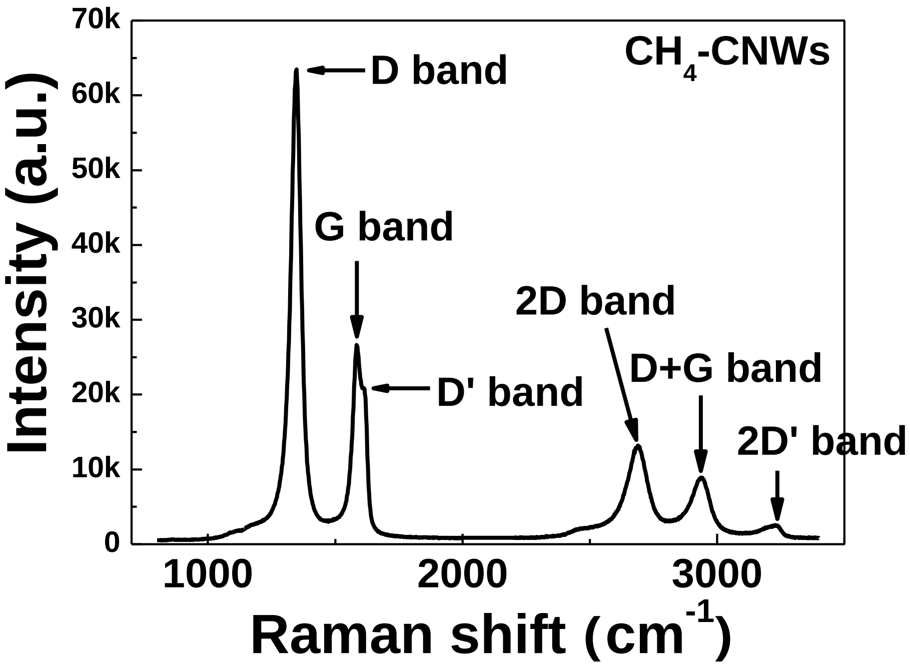
CF-CNWs 1



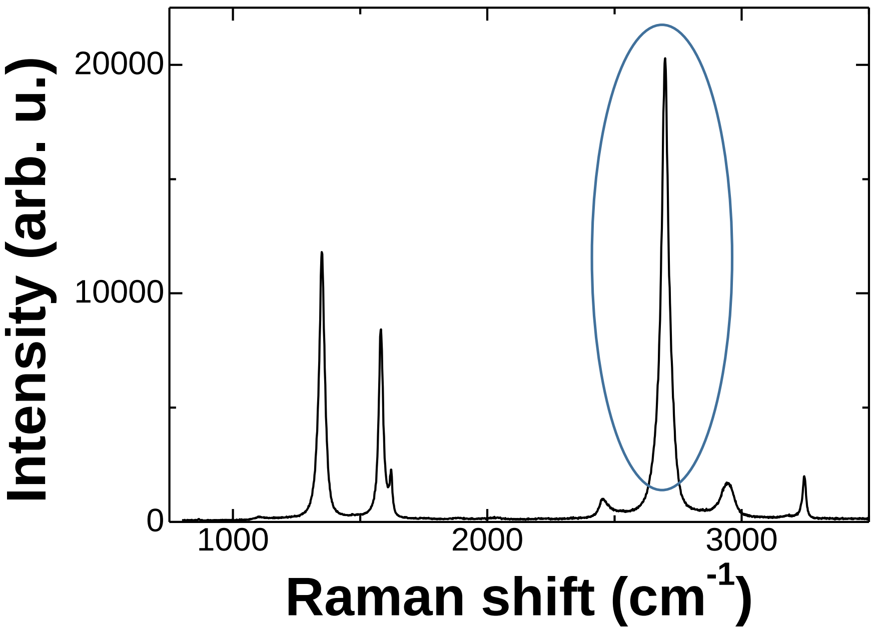
CF-CNWs 2



CH-CNWs Raman spectrum



CF-CNWs 1



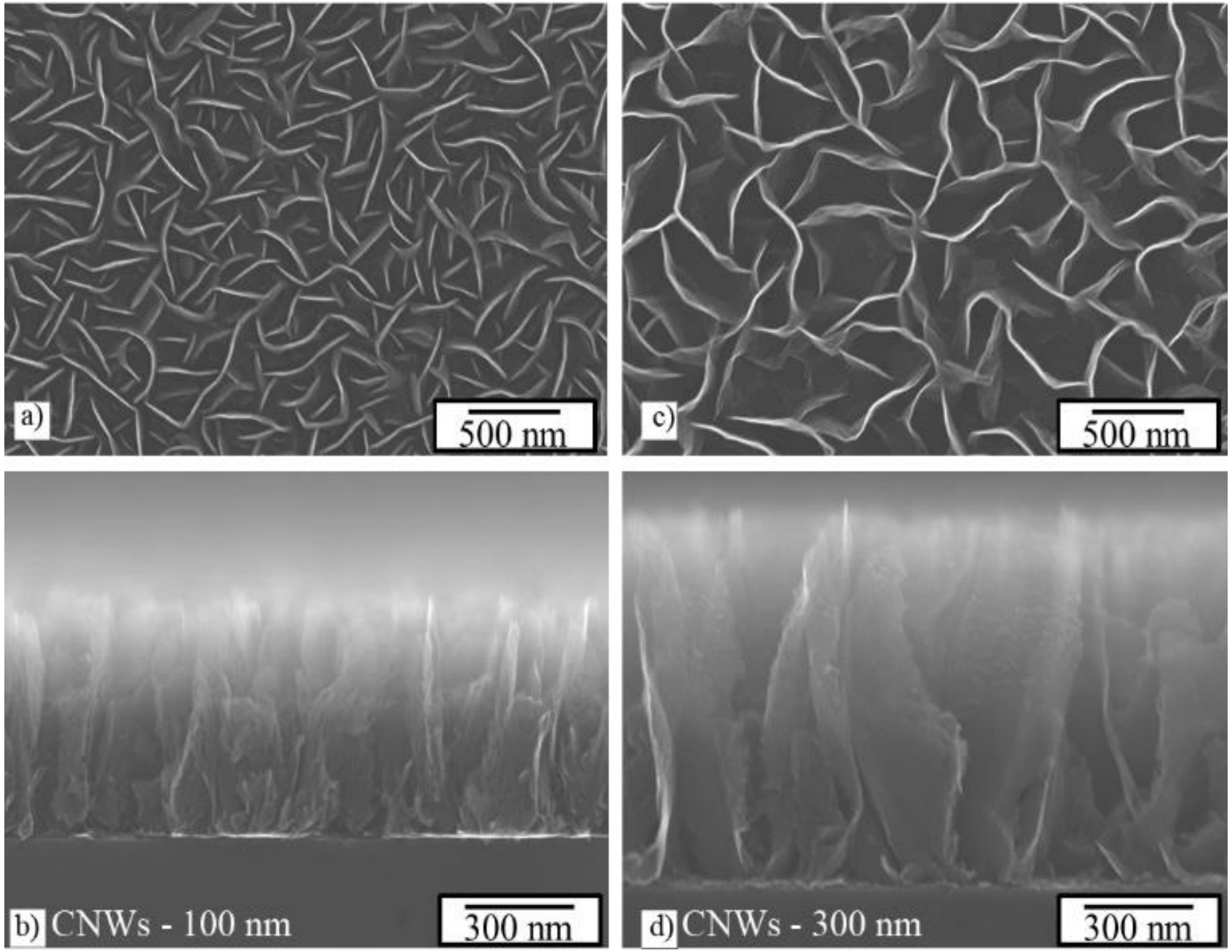
D band – 1328 cm^{-1}
G band – 1584 cm^{-1}
D’ band – 1620 cm^{-1}

2D band – 2685 cm^{-1}
D+G band – 2935 cm^{-1}
2D’ band – 3230 cm^{-1}

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

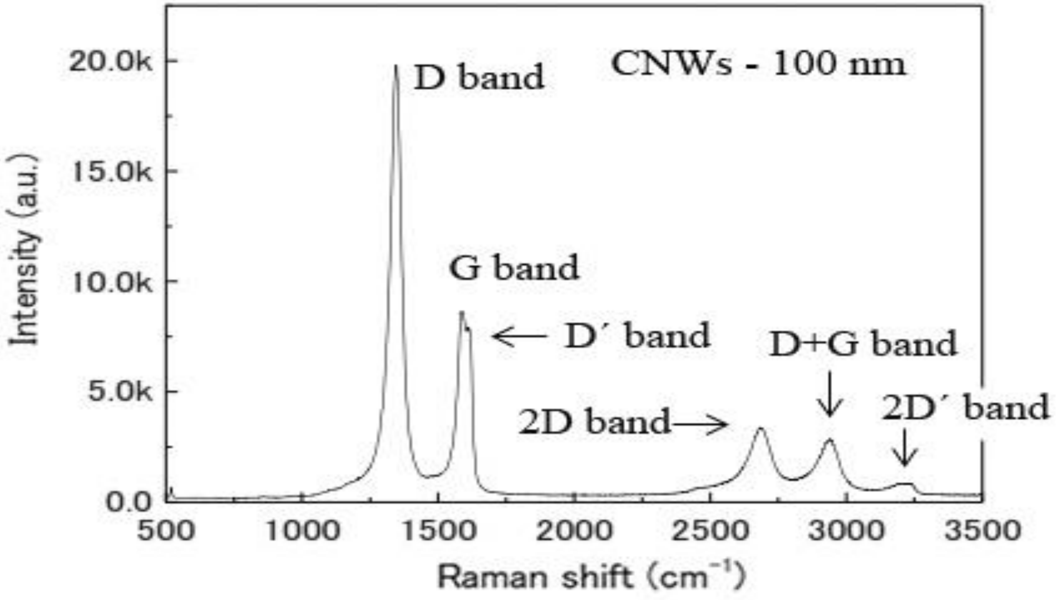


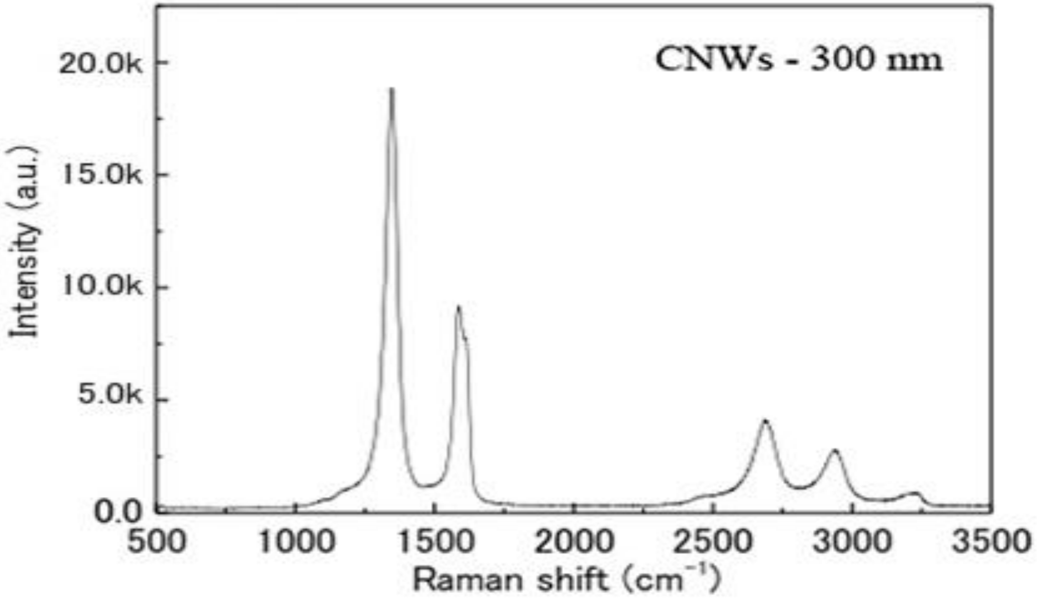
Differences between CNW

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.

Sample	$\frac{I_D}{I_G}$	$\frac{I_{D'}}{I_G}$	$\frac{I_{2D}}{I_G}$	I_D [cm^{-1}]	I_G [cm^{-1}]	$I_{D'}$ [cm^{-1}]	I_{2D} [cm^{-1}]
CNWs - 100 nm	2.29	0.91	0.40	1357	1597	1624	2693
CNWs - 300 nm	2.04	0.84	0.45	1334	1581	1607	2684

→ No obvious difference in material structure.



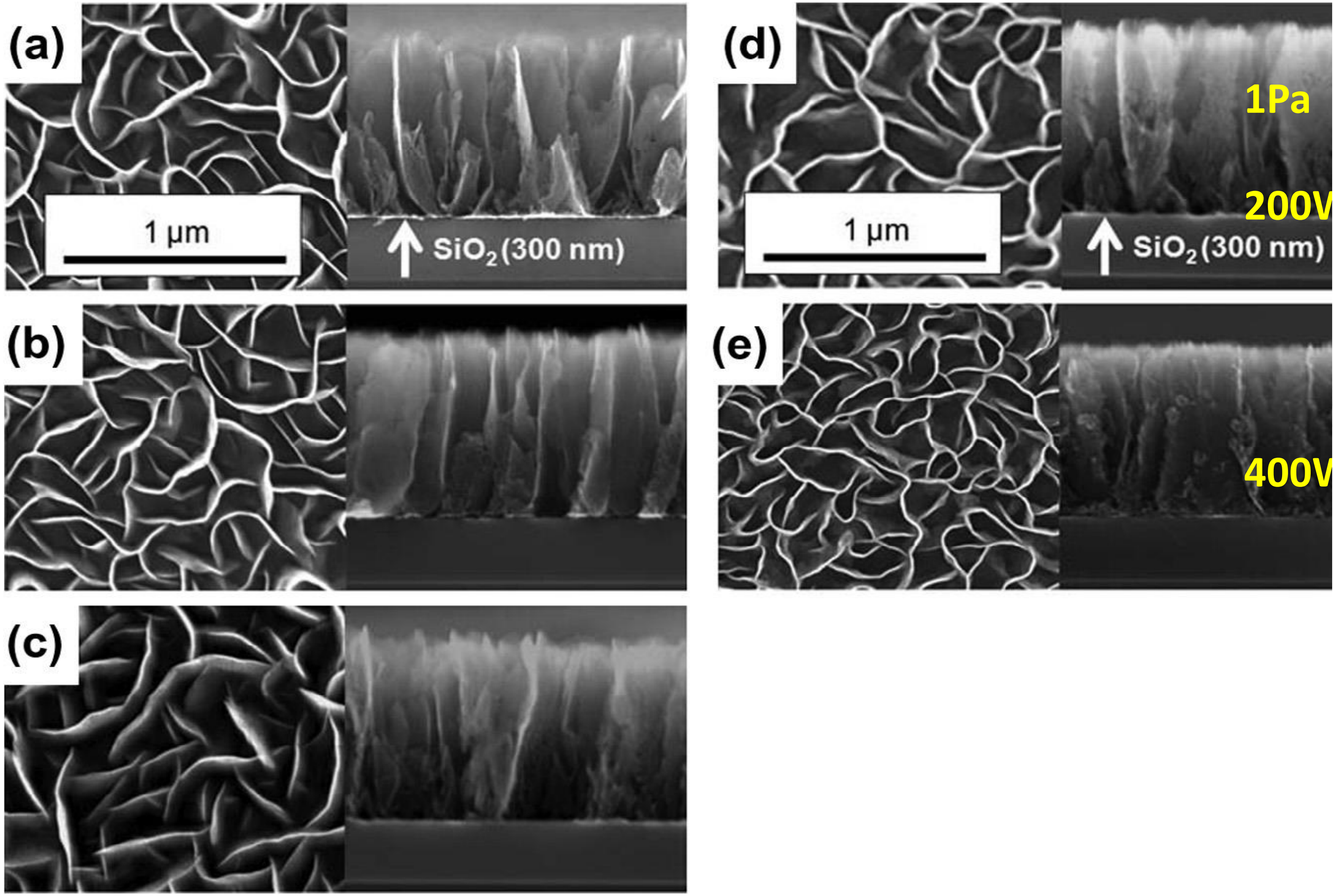


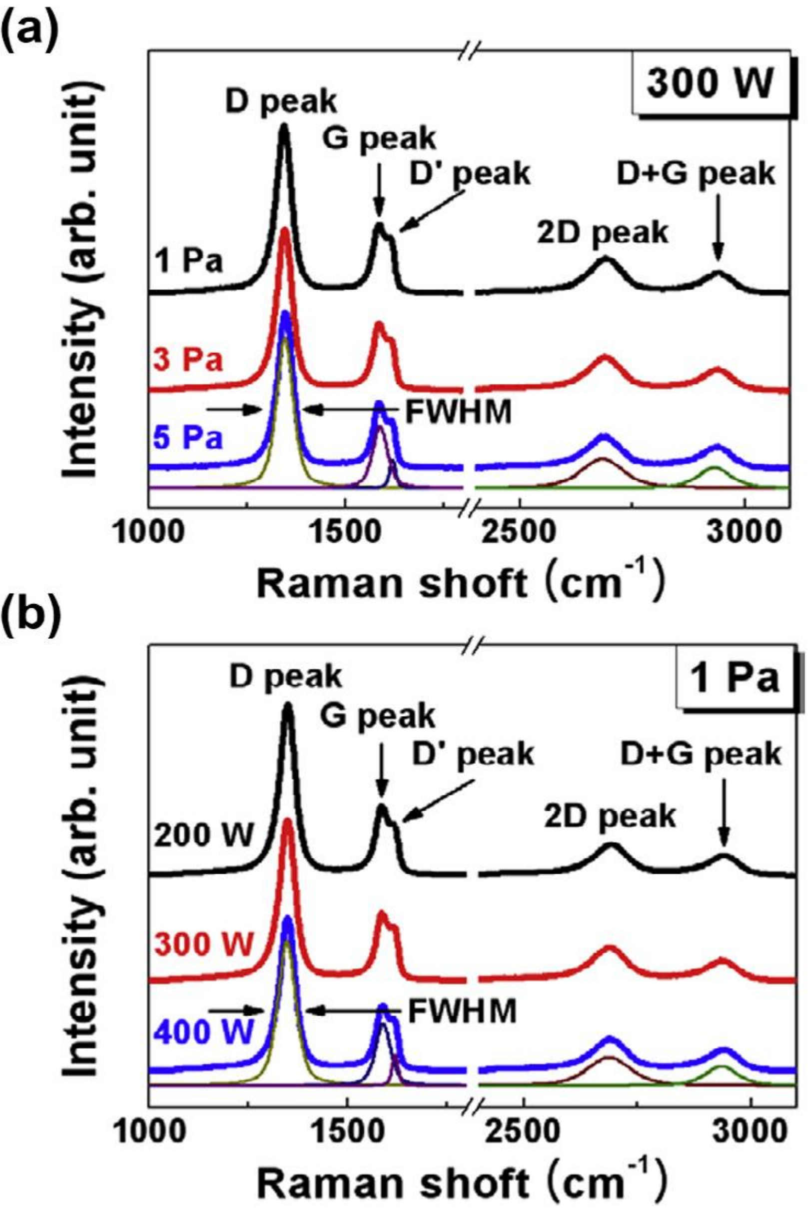
Growth of different CNW in CH4/H2

300W
1Pa

3Pa

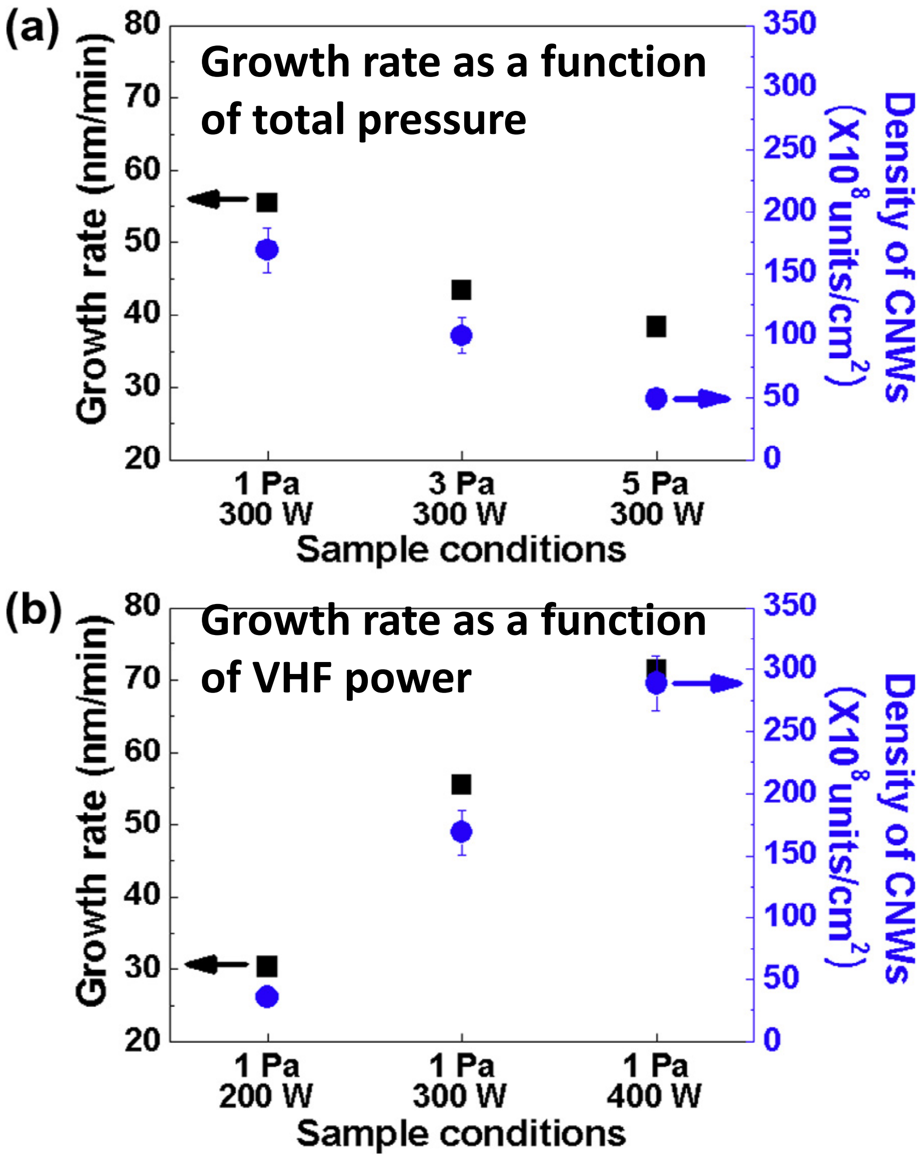
5Pa





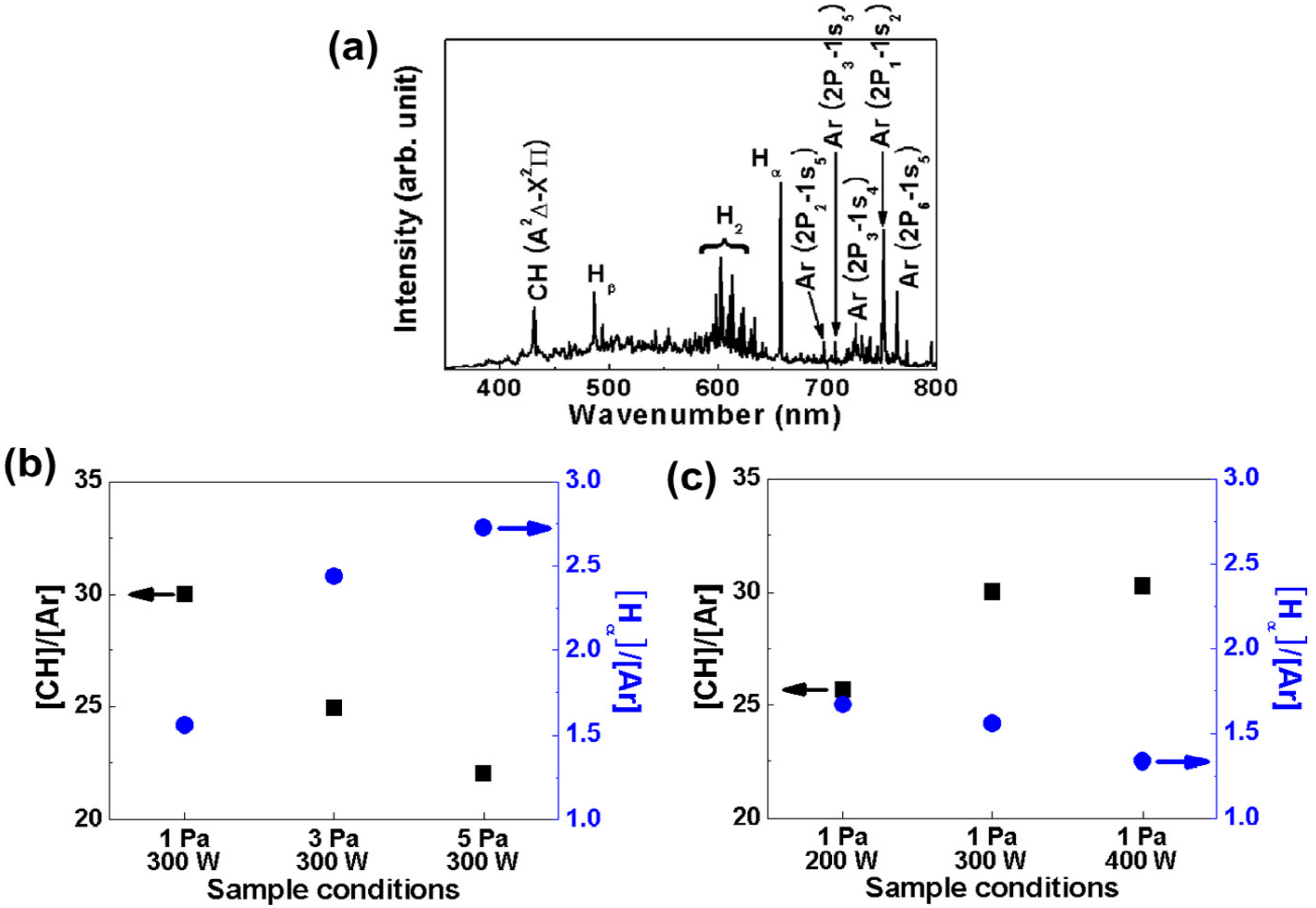
Cho, Kondo et al. Carbon, 2014, 68, 380-388.

Growth of CNW in CH4/H2 and radicals



Growth rate as a function of total pressure

Growth rate as a function of VHF power



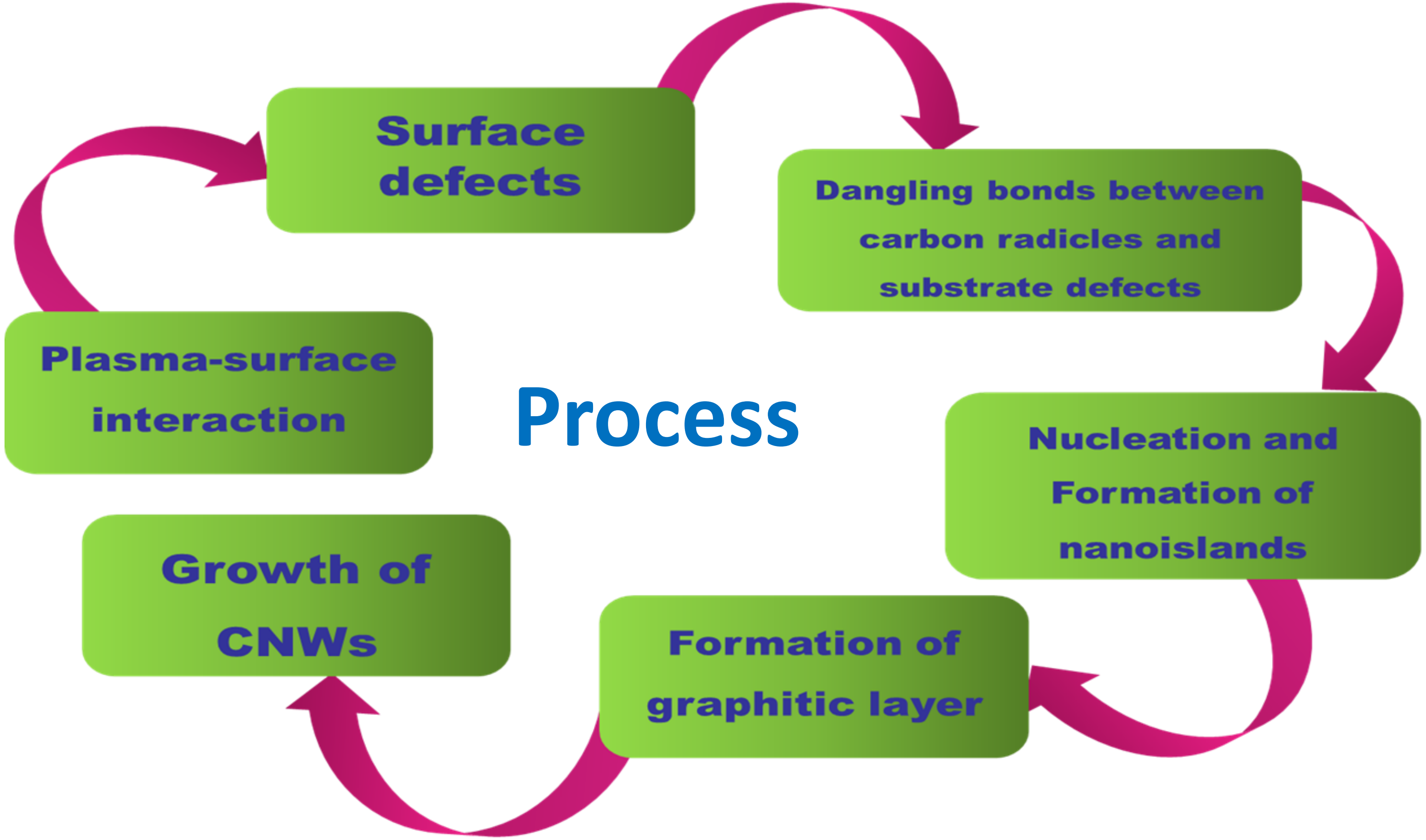
Where do we stand?

1) The **CNWs density is controlled by the total pressure**, and very-high-frequency CHF power as well as surface temperature.
2) No change in the crystal quality (Raman) and the chemical bonding states (XPS) is observed between CNWs
3) **H-atom density was linearly correlated with the wall density**.
4) RI-PECVD of CNWs the relative composition in CH and H atom is at least indicator of film quality control.
5) We think that **F atoms** from C2F6/H2 plasma might **act as a dopant** at the graphene edges. Consequently, electrical properties could be controled while maintaining the crystal quality and chemical bonding state.

Role of substrate and effect of catalyst

Substrate materials

- Transition metal substrates
- Dielectric substrates
- Cylindrical substrates



Surface defects

Dangling bonds between carbon radicles and substrate defects

Nucleation and Formation of nanoislands

Formation of graphitic layer

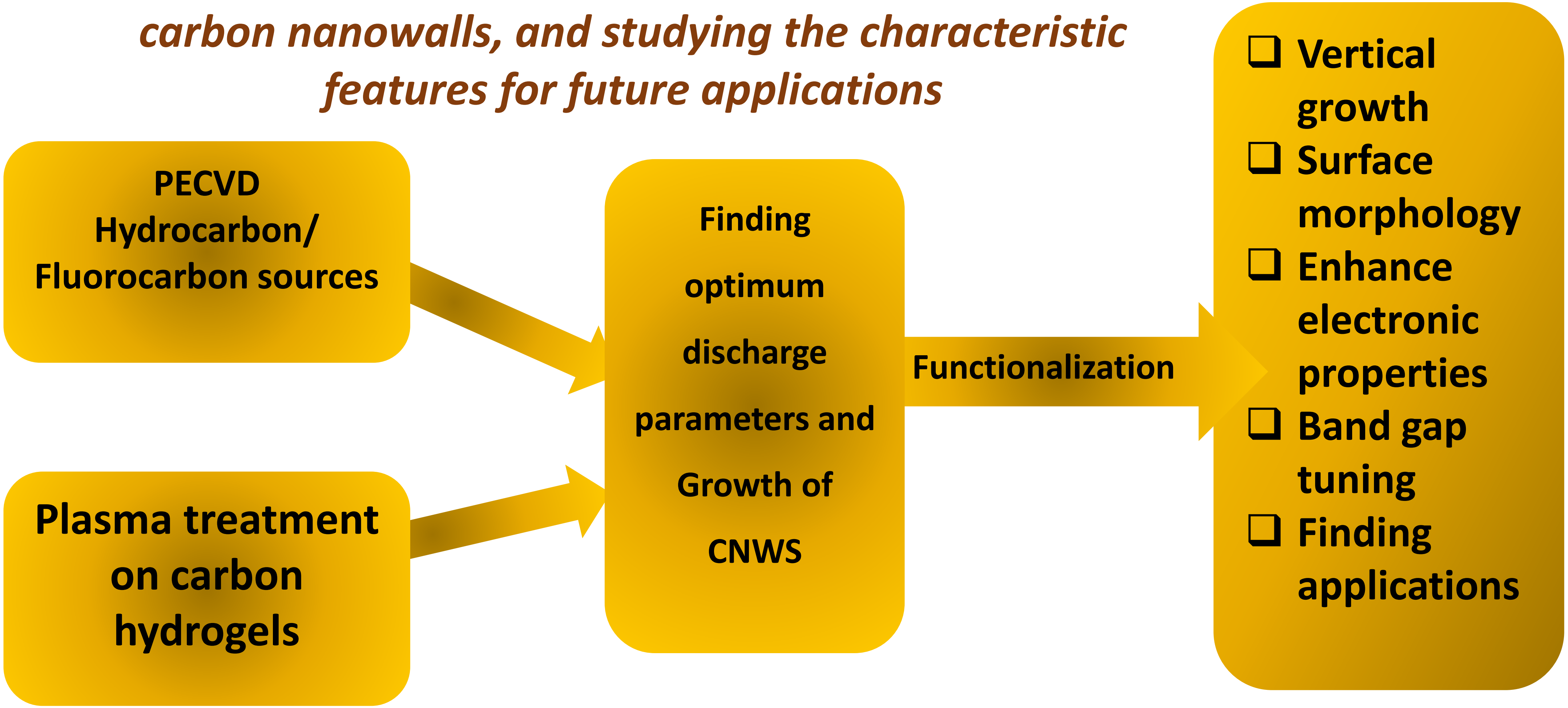
Growth of CNWs

Plasma-surface interaction

Process

Conclusions

Growth and processing of vertically aligned 2D carbon nanowalls, and studying the characteristic features for future applications



PECVD Hydrocarbon/ Fluorocarbon sources

Plasma treatment on carbon hydrogels

Finding optimum discharge parameters and Growth of CNWS

Functionalization

- ☐ **Vertical growth**
- ☐ **Surface morphology**
- ☐ **Enhance electronic properties**
- ☐ **Band gap tuning**
- ☐ **Finding applications**