2nd Dissemination Workshop on Membrane Technology for Water Reclamation

Dorsett Kuala Lumpur Hotel, Kuala Lumpur

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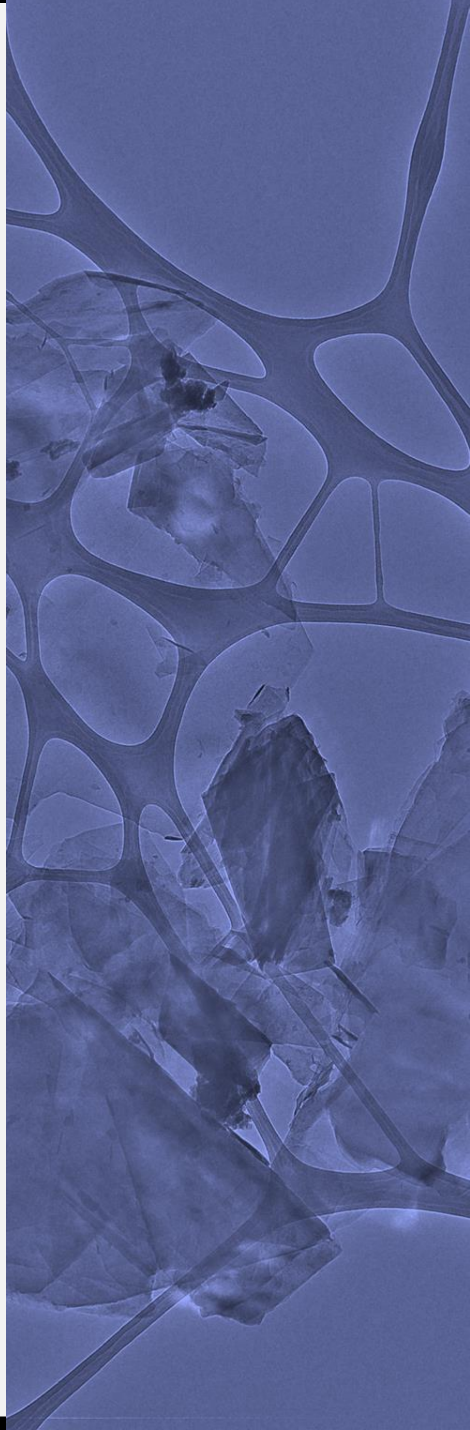
Universiti Teknologi Malaysia.

DEVELOPMENT OF ADVANCED GRAPHENE MEMBRANE

MyMembrane
MALAYSIA MEMBRANE SOCIETY



ABOUT ME

-Born in Negeri Sembilan

-Hometown in Malacca

-Work in UTM JB, Johor

-Obtain my D. Eng (Frontier Materials) from Nagoya Institute of Technology, Japan in 2013. Nagoya is my second hometown, been almost 11 years in Japan (2004-2015).

-Associate Fellow in AMTEC, UTM.

-Previous research works related on "Room temperature growth of Carbon Nanofibers", "Development of Field emission Emitters", "Fabrication of metallic nanomaterials using ion irradiation technique" and Fundamental studies of Graphene formation using In Situ Transmission Electron Microscope".

-Current research related on carbon nanomaterials fabrication, fundamental studies of graphene growth, development of graphene based membrane and its characterization.

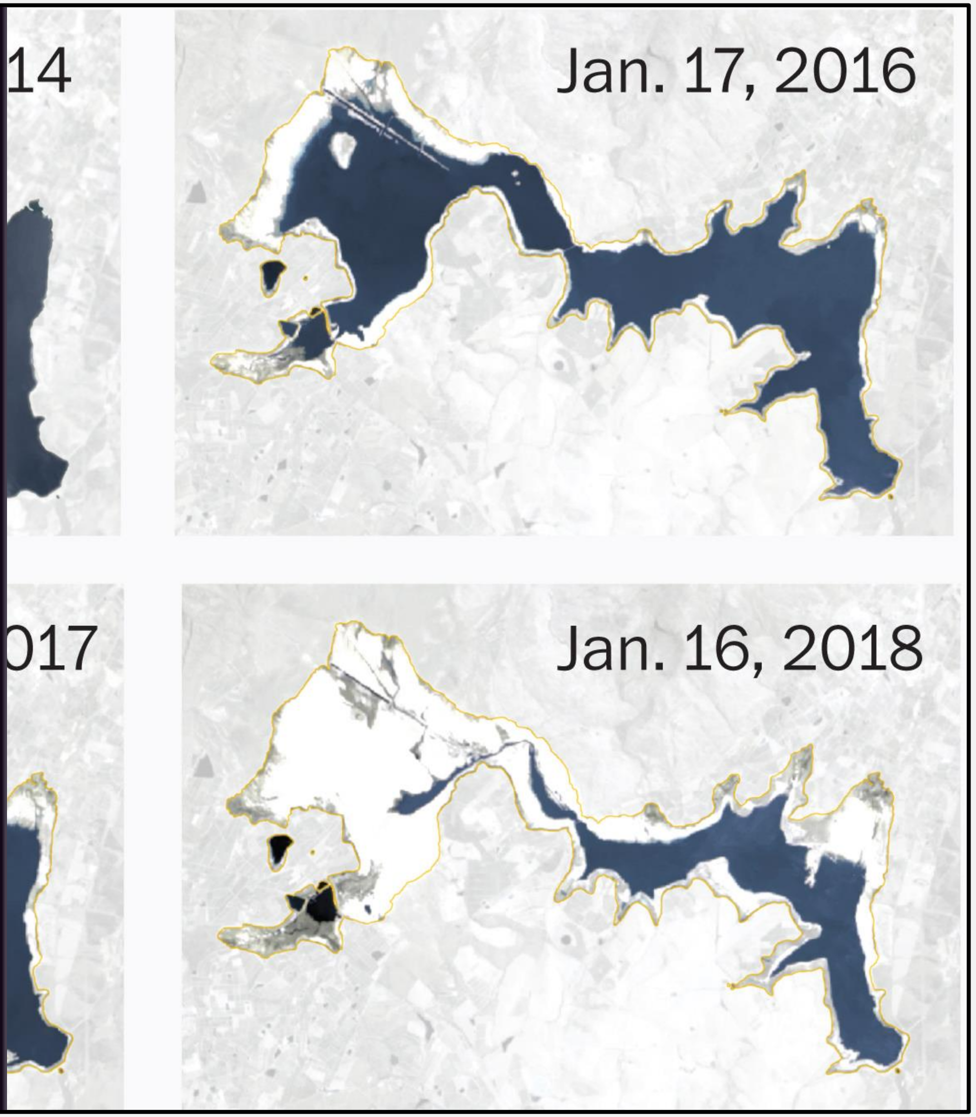
OUTLINE

- Membranes Materials for Sea Water Desalination Process
- Graphene Membranes
- Atomic Structure of Graphene
- Modification of Graphene Structure
- Ion Irradiation Treatment
- Hydrogen Etching at High Temperature
- Research Approach – Synthesis of Graphene
- Chemical Vapor Deposition, Activated Carbon Technique
- Graphene Formation in CVD
- Determine Graphene Layers using Raman Spectroscopy
- Current results – Low Temperature Growth of Graphene using CVD
- Raman Mapping
- Summary

MEMBRANE MATERIALS FOR DESALINATION PROCESS

Clean Water Crisis

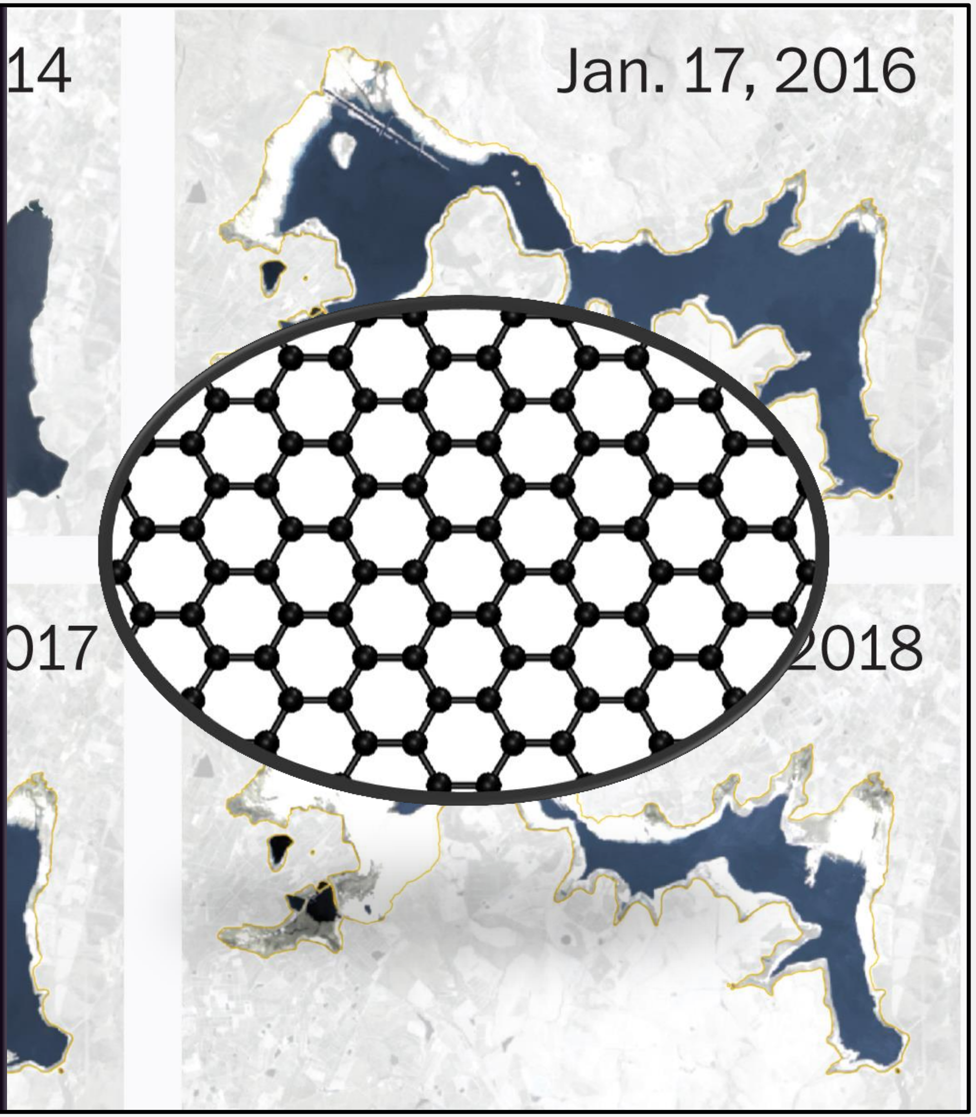
Ceramic hollow membrane



MEMBRANE MATERIALS FOR SEA WATER DESALINATION PROCESS

Clean Water Crisis

Ceramic hollow membrane



GRAPHENE MEMBRANES

Graphene excel on thermal and chemical stability.

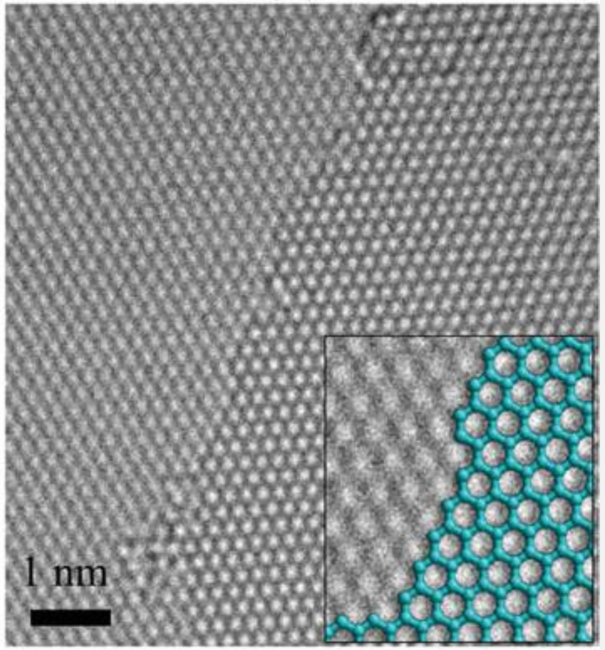
Advantages for high temperature or strong acidic/alkaline separation medium with high stability.

Pristine graphene have been proved to stop helium, only allowed protons to permeate its structure. The impermeability of graphene for molecules makes it is applicable as a barrier layer for gases and liquids, or to protect metallic surfaces against corrosion.

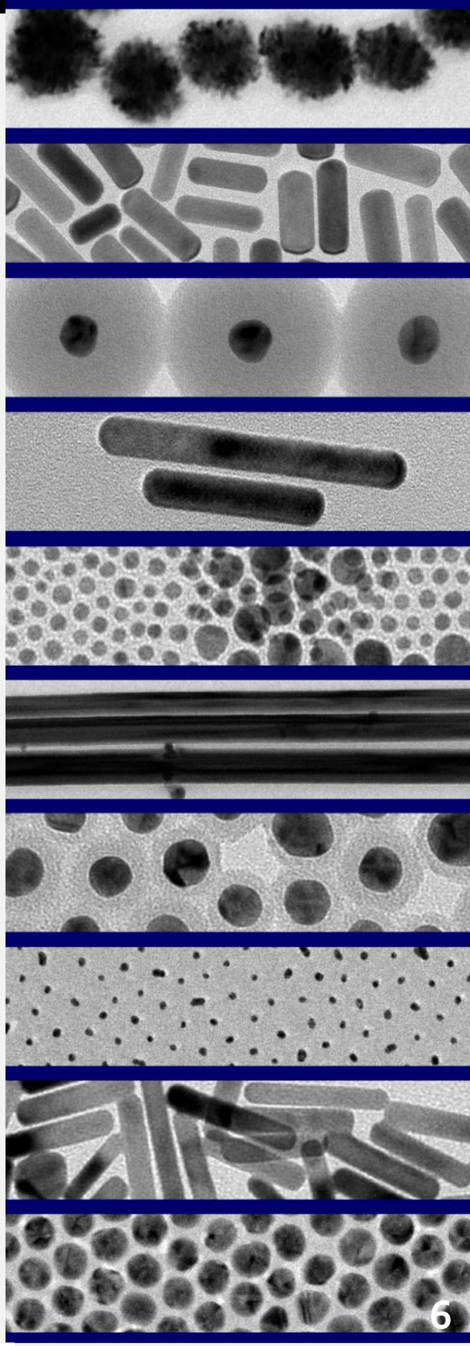
Graphene has to be functionalized with nanopores or nanochannels through chemical or physical approaches.

Pristine graphene (crystalline) Graphene oxide(amorphous)

Prof. Sir Andre Geim, Manchester University

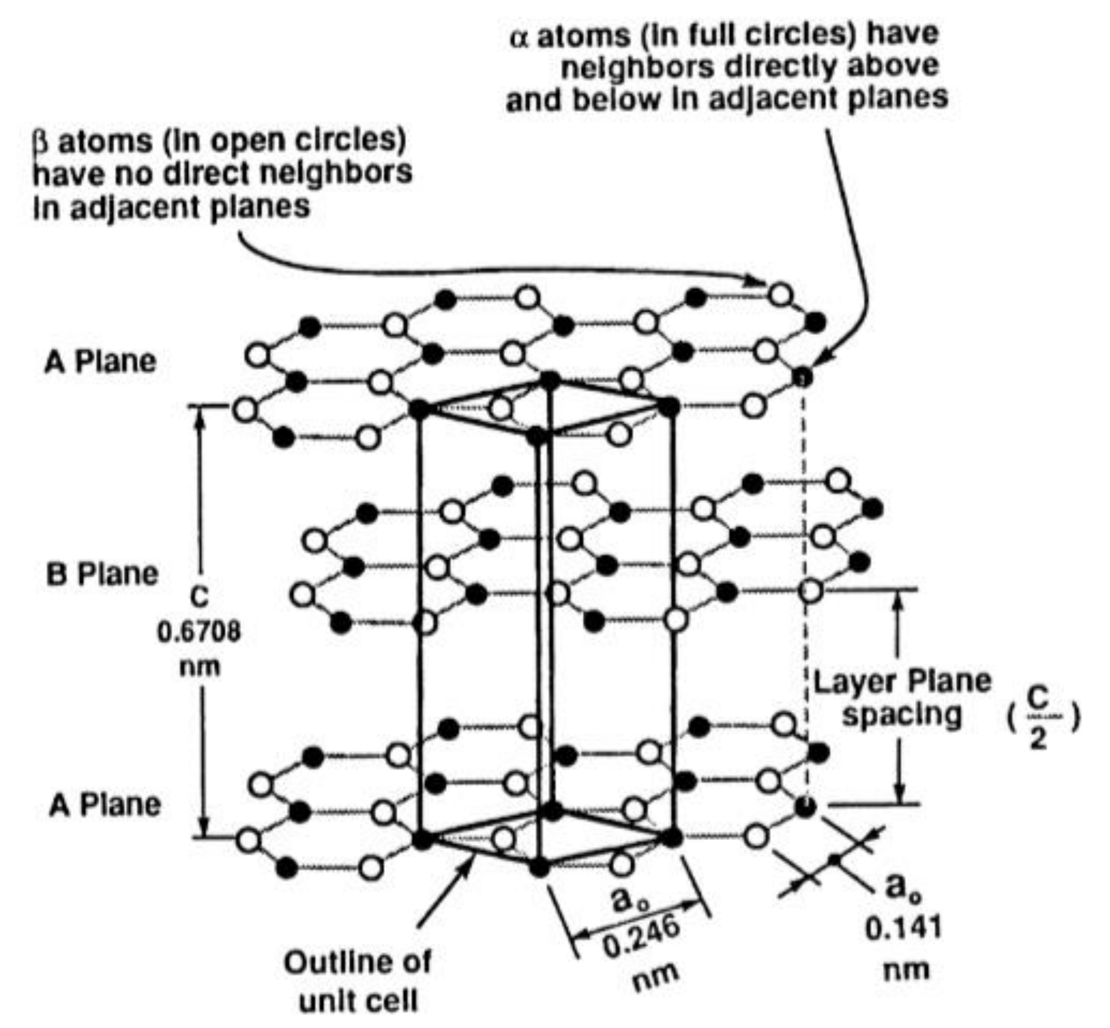


Graphene under HRTEM, SMALL (10), 14, 2766, 2014.



ATOMIC STRUCTURE OF GRAPHENE

- 1st 2D atomic crystal
- Monolayer of *sp*^{2} bonded carbon atoms
- Arranged in honeycomb network
- Carbon-Carbon bond length is about 0.142 nm
- Mother of graphitic forms
- The interplanar spacing (d spacing) between two layers of graphene is **about 0.3354 nm.**

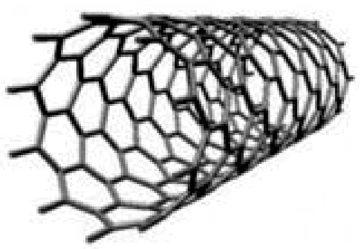


MALAYSIA MEMBRANE SOCIETY

ALLOTROPES OF CARBON

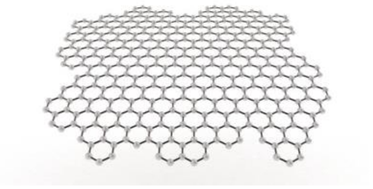
Fullerene

1) **0D** carbon atom
2) Known as Bucky ball
3) Biomedical, sporting goods



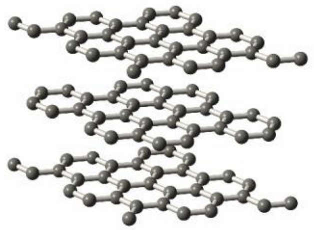
CNT

1) **1D** carbon atom
2) rolled up form of graphene
3) Polymers conductor, anti-static packaging



Graphene

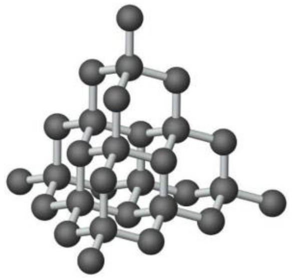
1) **2D** carbon atom
2) densely packaged in a honeycomb-shape crystal lattice
3) Electronic, gas separation, membrane



Graphite

1) Multilayer of graphene
2) Most stable among other allotropes
3) Electrical conductor, membranes

Amorphous



Diamond

1) **3D** carbon atom
2) High hardness and high dispersion of light
3) polishing, cutting grinding
4) jewelry

APPLICATIONS OF GRAPHENE

Graphene

Chemical Field
- Plastic additives
- Rubber additives
- Nanofluid
- Catalyst support

Medical Field
- Drug delivery
- Sensor for cancer therapy
- Smart plaster

Structural field
- Membranes
- Composite filler
- Composite matrix
- Protective coating

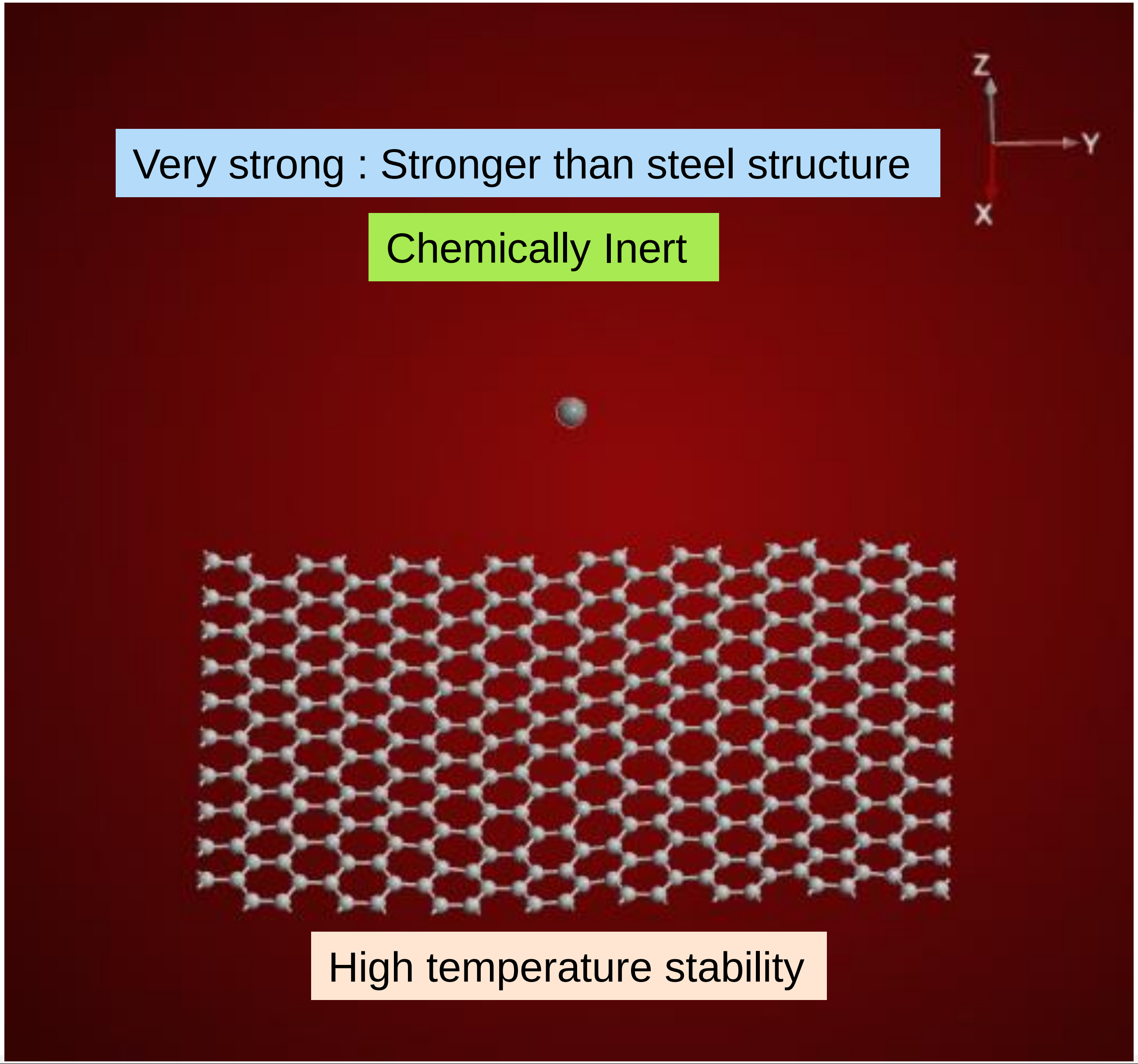
Energy Field
- Lithium-ion batteries
- Support material for platinum catalyst in fuel cells
- Ultra-capacitors
- Solar cell

Electronic field
- Transparent electrode
- Photodetector
- Memory chips

(National Graphene Action Plan 2020; M. Pepolow, 2013; K. Novoselov *et al*., 2012)

MODIFICATION OF GRAPHENE STRUCTURE

Physical approaches



Plasma Treatment

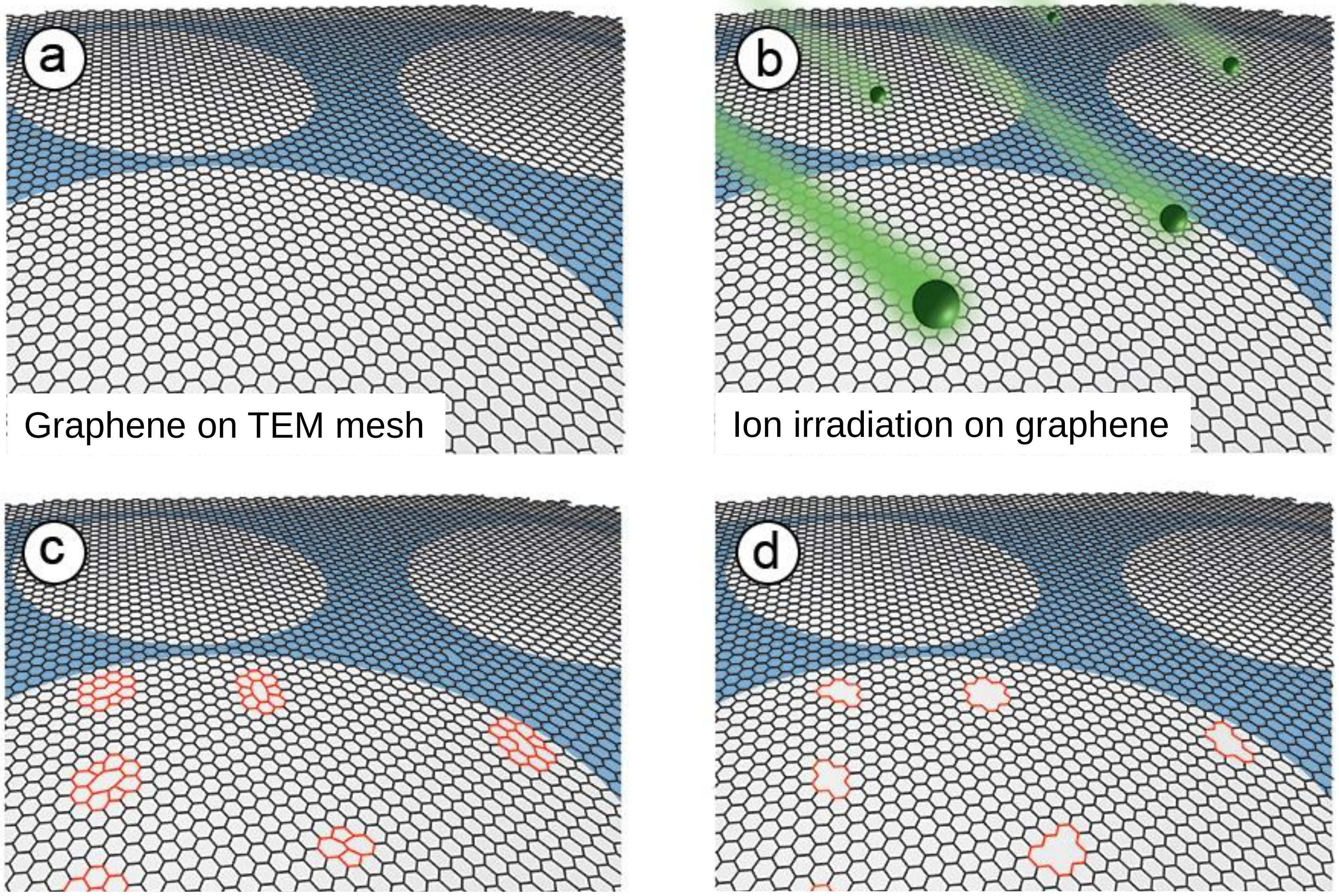
Oxygen

Gallium

MALAYSIA MEMBRANE SOCIETY

ION IRRADIATION TREATMENT

Physical approaches



Creating defects on graphene structure

Defects creating an opening or nanoporous

e^-

N_2^+

Ar^+

Xe^+

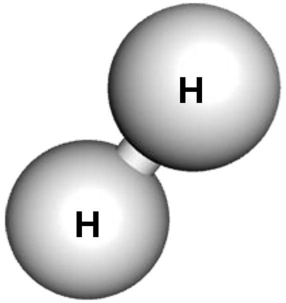
Irradiation time

Ion size

HYDROGEN ETCHING AT HIGH TEMPERATURE

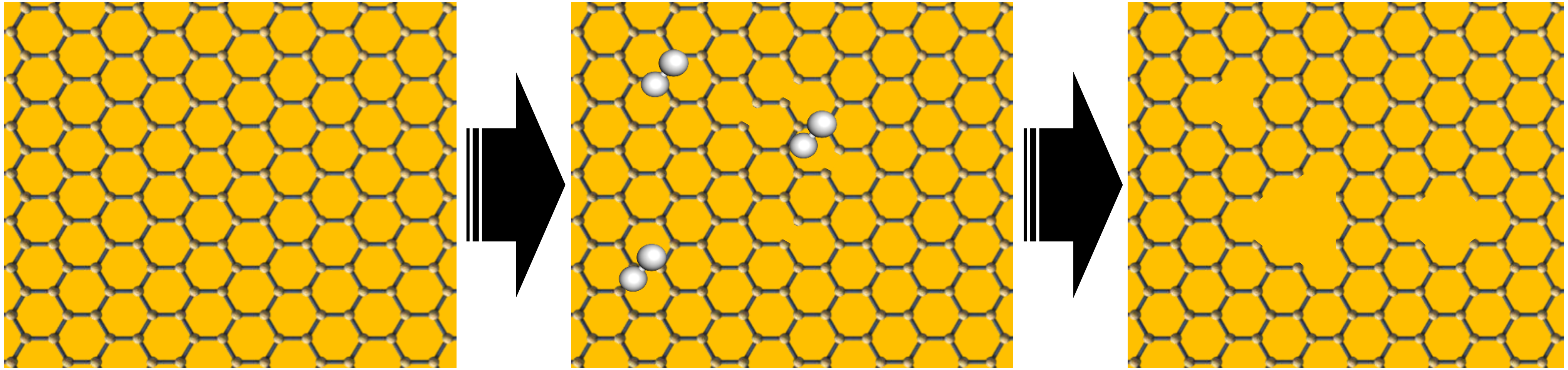
Chemical approaches

Hydrogen atmosphere



High temperature : > 900 °C

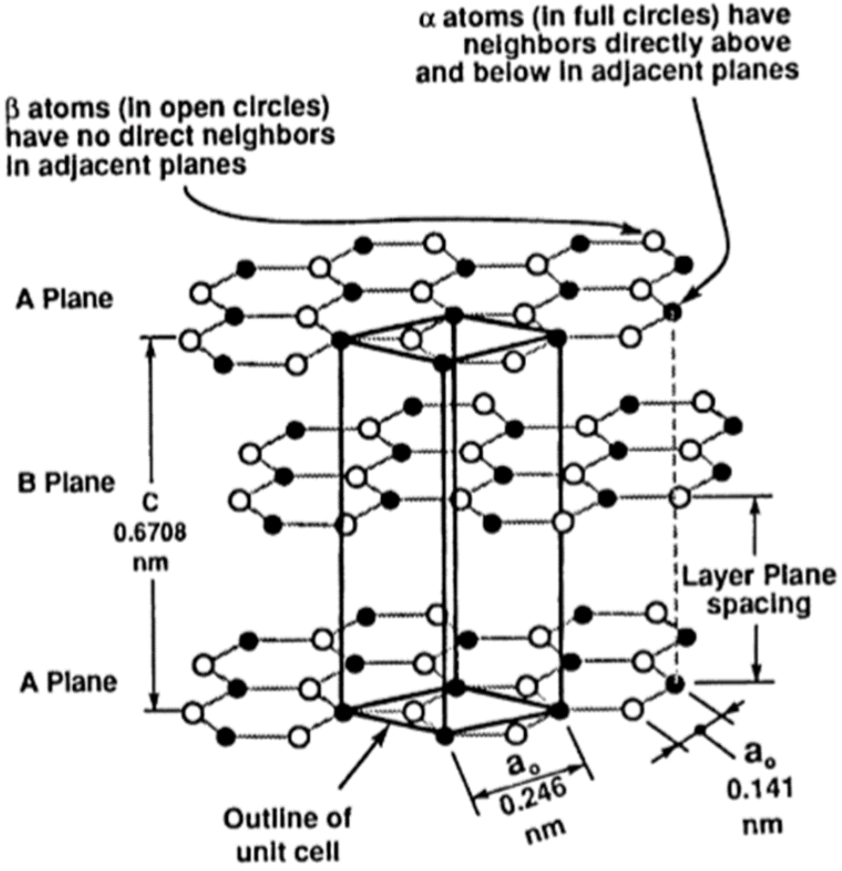
$$2H_2 + C \underset{}{\overset{Cu}{\rightleftharpoons}} CH_4$$

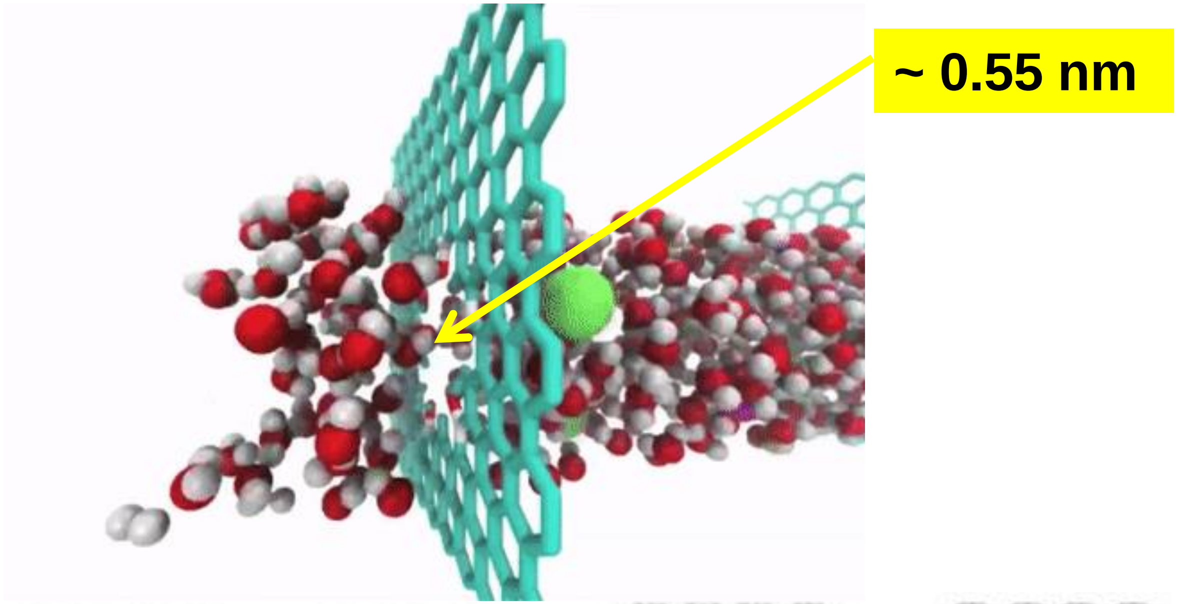


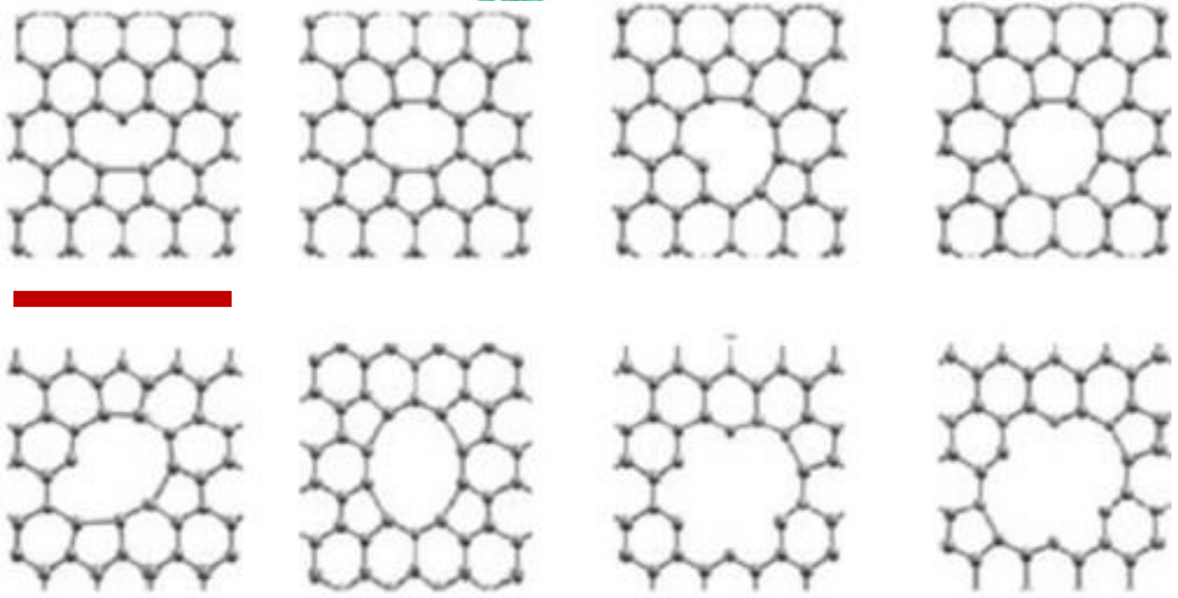
Exposure time

Flow rate

NANOPOROUS SIZE FOR WATER PERMEABILITY

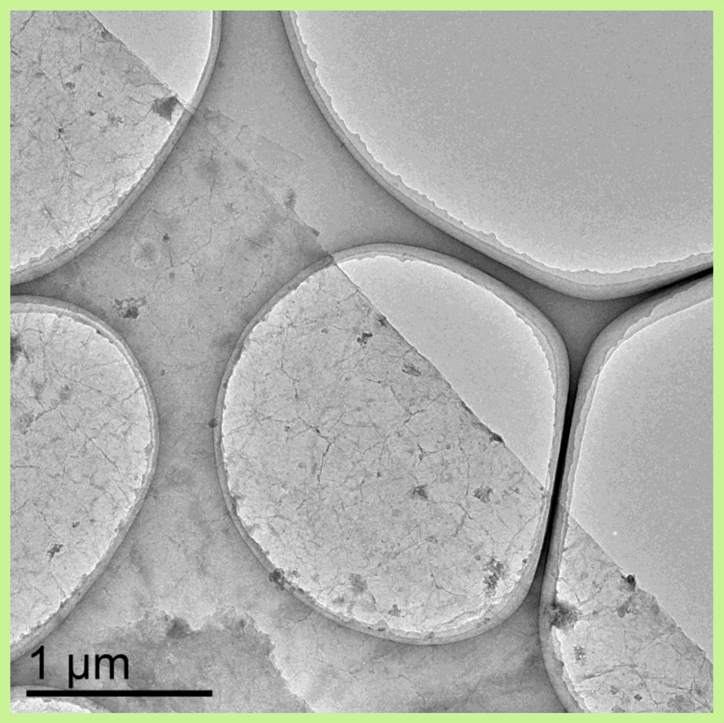
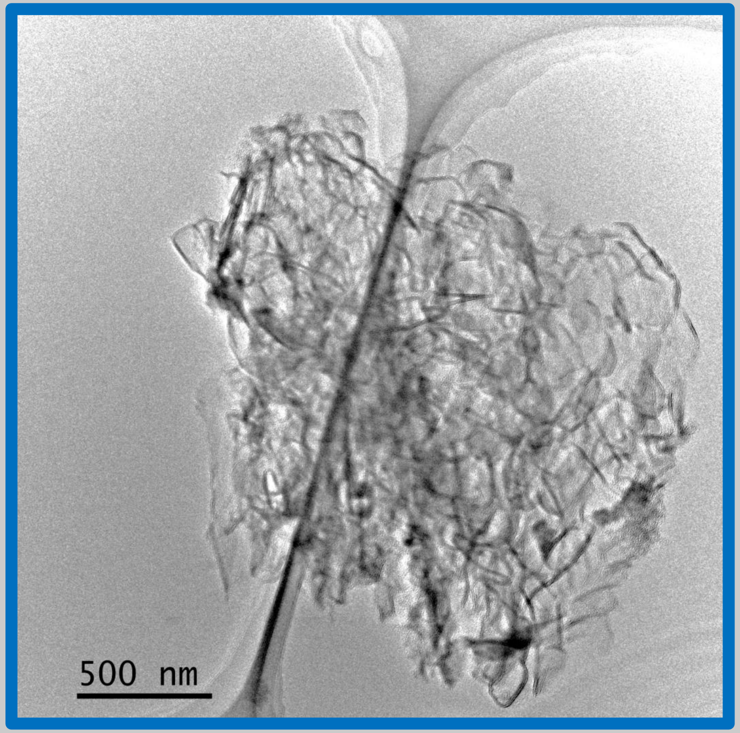






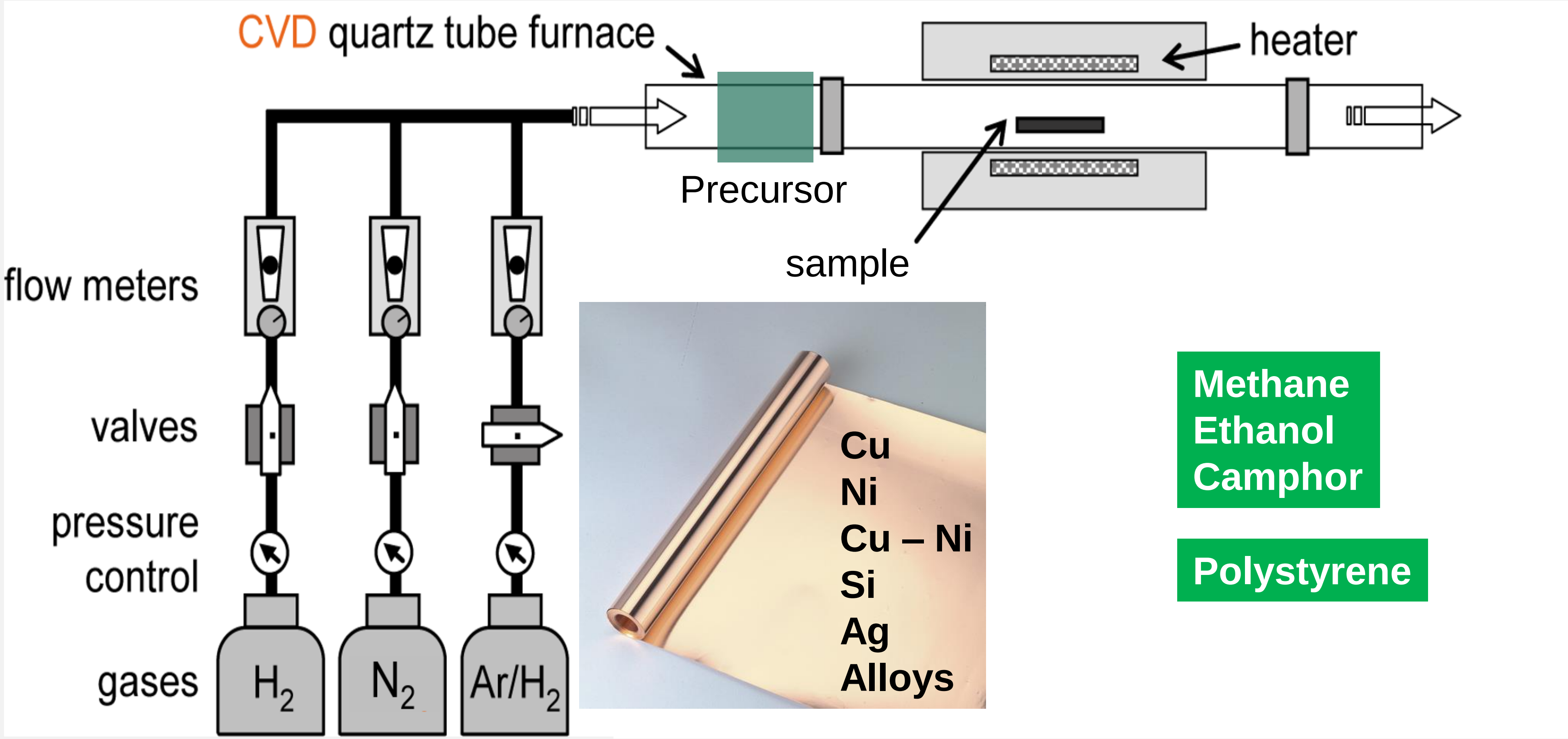
RESEARCH APPROACH

Many technique with slightly different types of graphene

Chemical vapor deposition (CVD)	Activated carbon technique
	
1 - 5 layers graphene	Multilayers (10 ~) graphene
900 °C (300 ~ 1000 °C, depend upon precursor)	800 ~ 950 °C
Nitrogen/Argon Atmosphere	Ambient Atmosphere

RESEARCH APPROACH

Chemical Vapor Deposition (CVD)

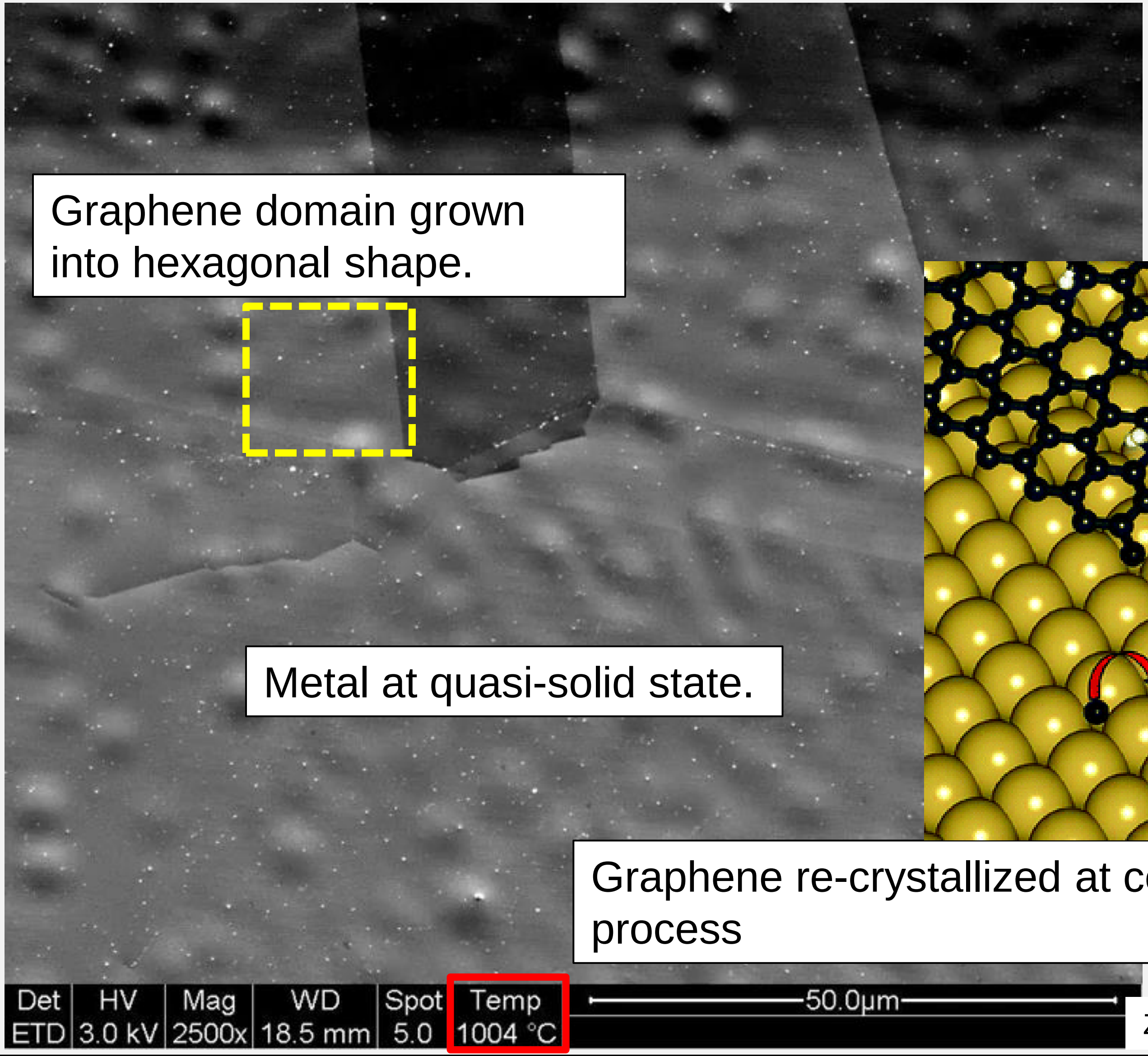


Methane
Ethanol
Camphor

Polystyrene

RESEARCH APPROACH

Chemical Vapor Deposition (CVD)



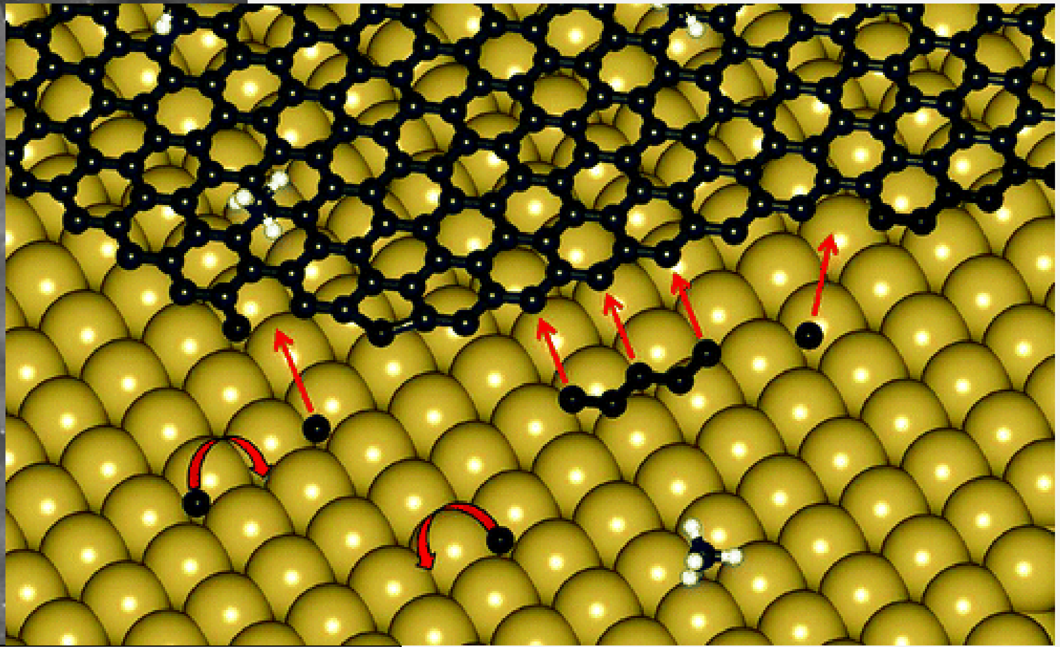
Graphene domain grown into hexagonal shape.

Metal at quasi-solid state.

Deposition time

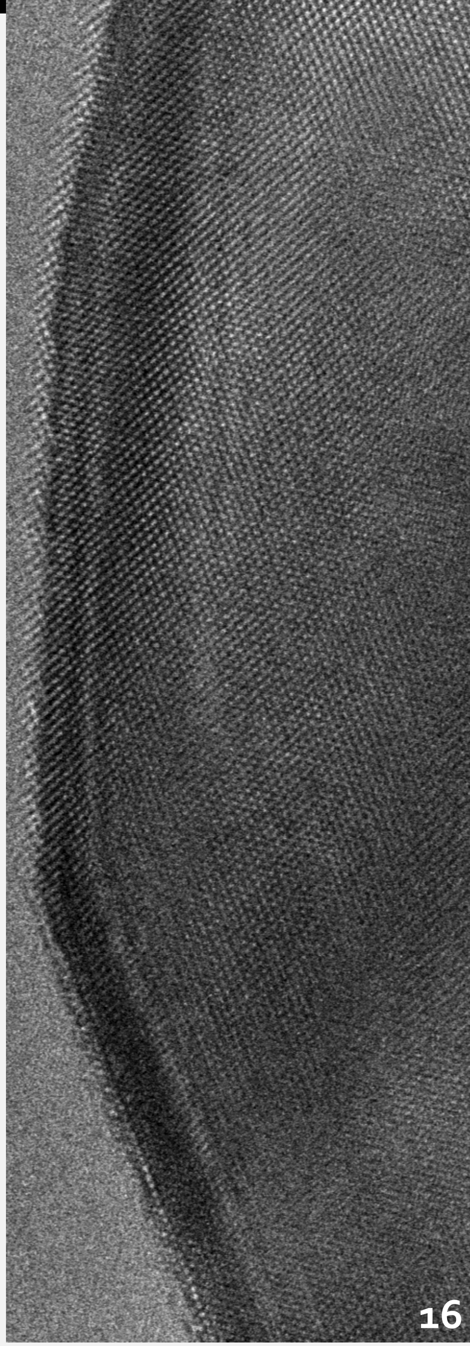
Growth temperature

Catalyst species

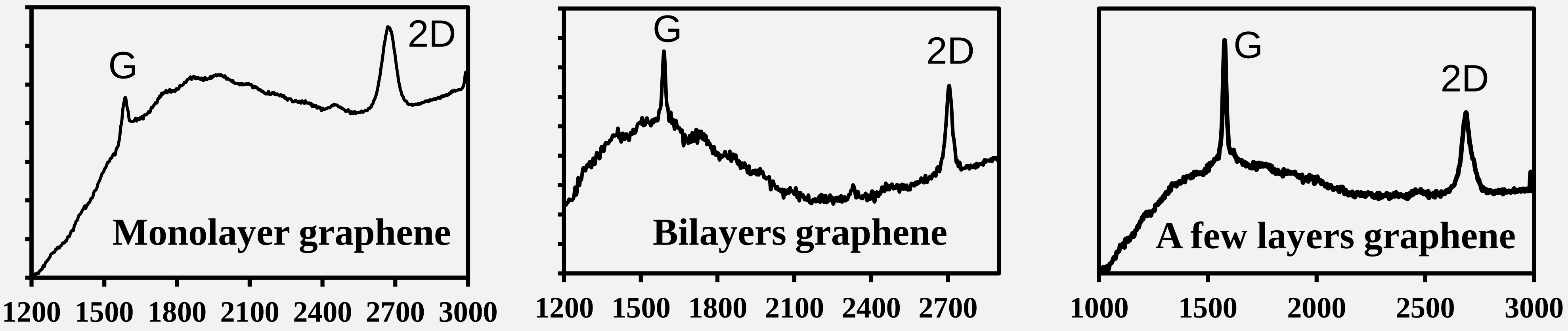


Graphene re-crystallized at cooling process

Z. J. Wang *et al.* ACS Nano, 2015, 9 (2), pp 1506–1519



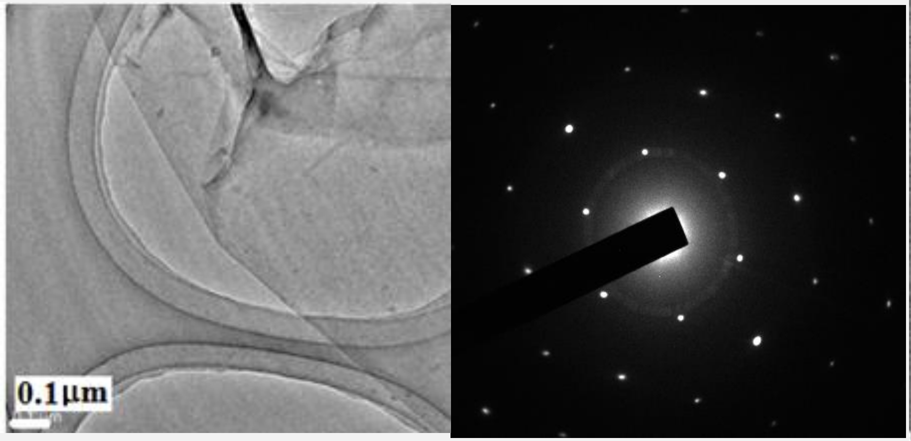
RAMAN ANALYSIS ON DIFFERENT NUMBER OF GRAPHENE LAYERS



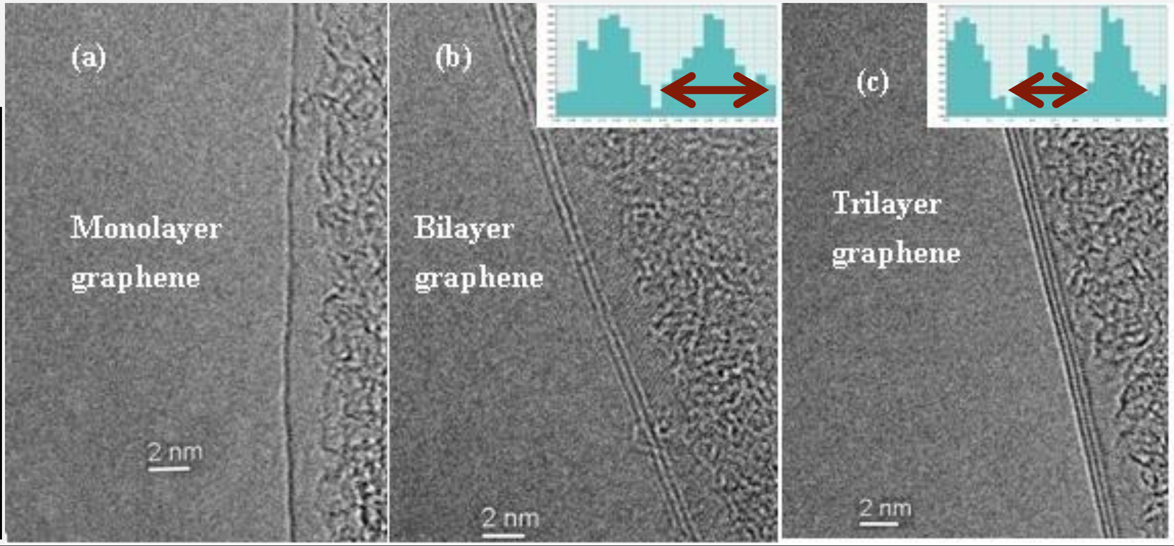
TEM analysis of different number of graphene layers

Chemically etching the Cu foil using nitrate solution.

Transfer on TEM mesh.

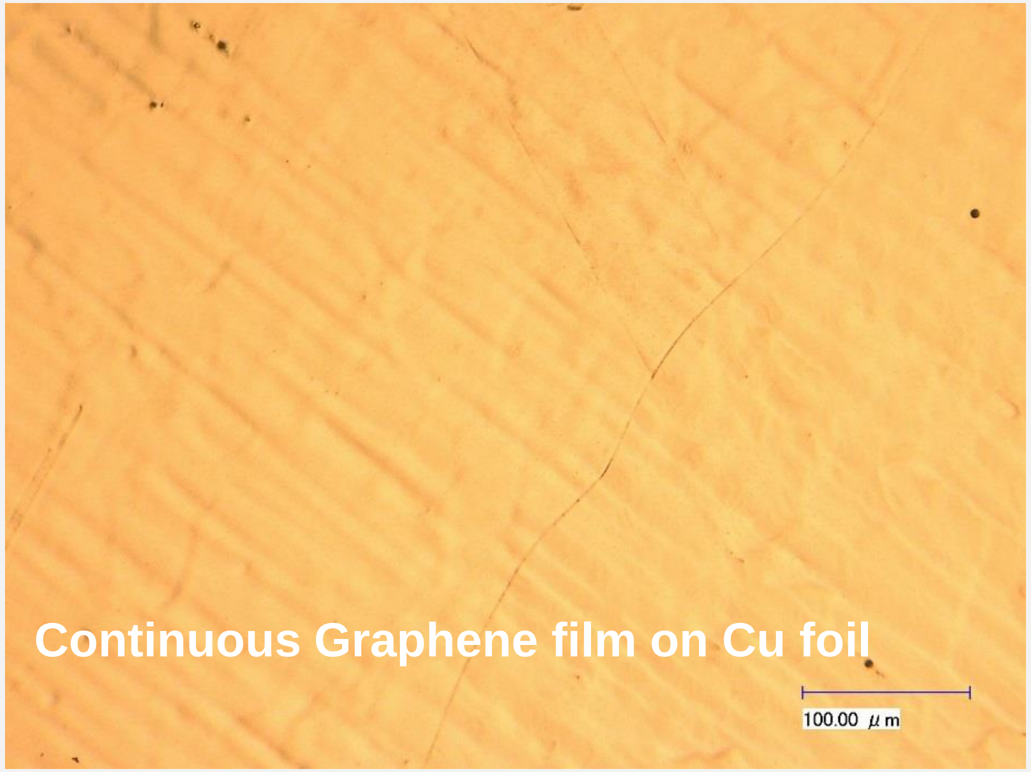


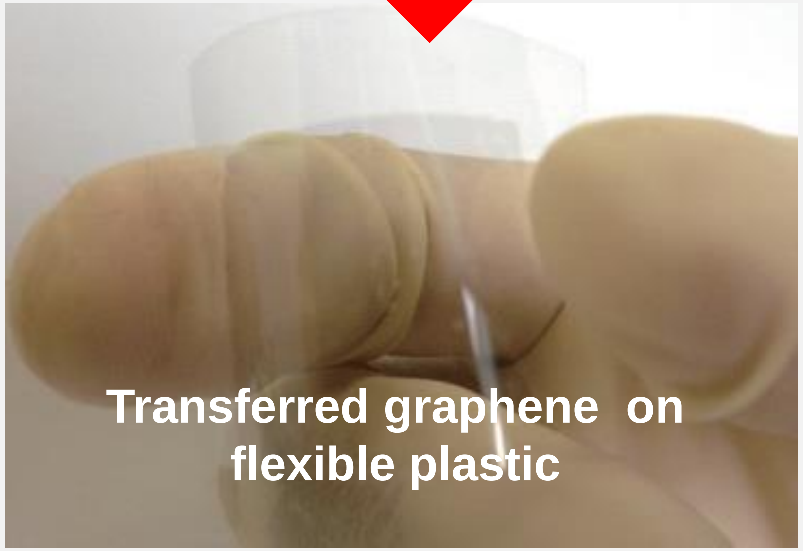
~ 0.3345 nm



PREVIOUS PROJECT

Camphor, Temp.: 850 °C, Catalyst: Copper





Kalita, et al. *J. Mat. Chem., 20, 9713 (2010);* Kalita et al., *J. Mater. Chem., 21, 15209 (2011)* Hirano, Kalita, Tanemura et al. Nanoscale, 4, 7791 (2012); Kalita, Tanemura et al. *J. Phys. D: Appl. Phys., 46, 455103 (2013)*

NITech, JAPAN

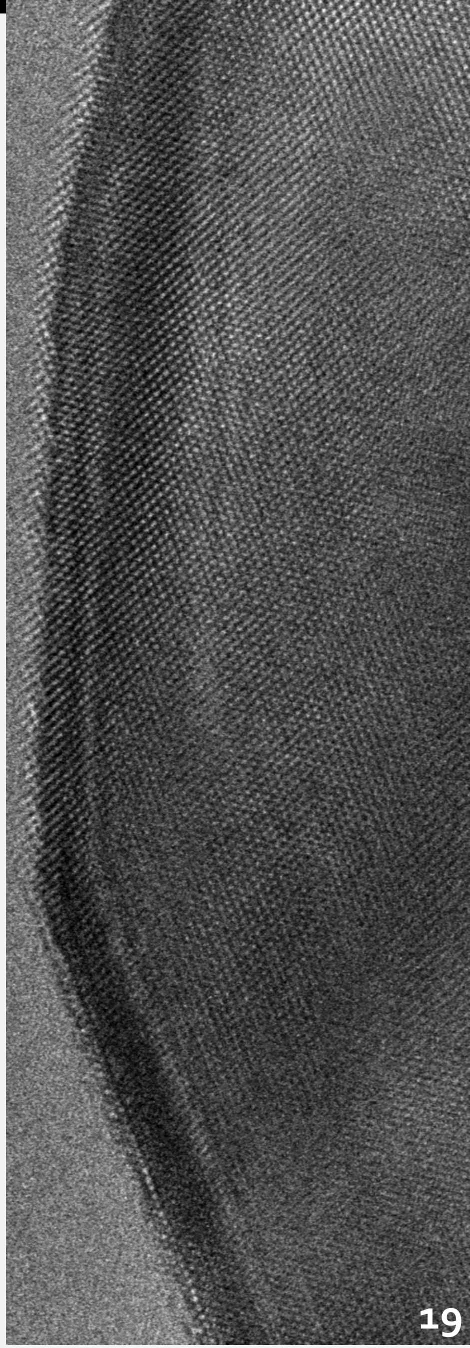
GRAPHENE GROWTH AT HIGH TEMPERATURE IS TOO MAINSTREAM

Synthesis of graphene at low temperature.

What are the advantages of low temperature graphene?

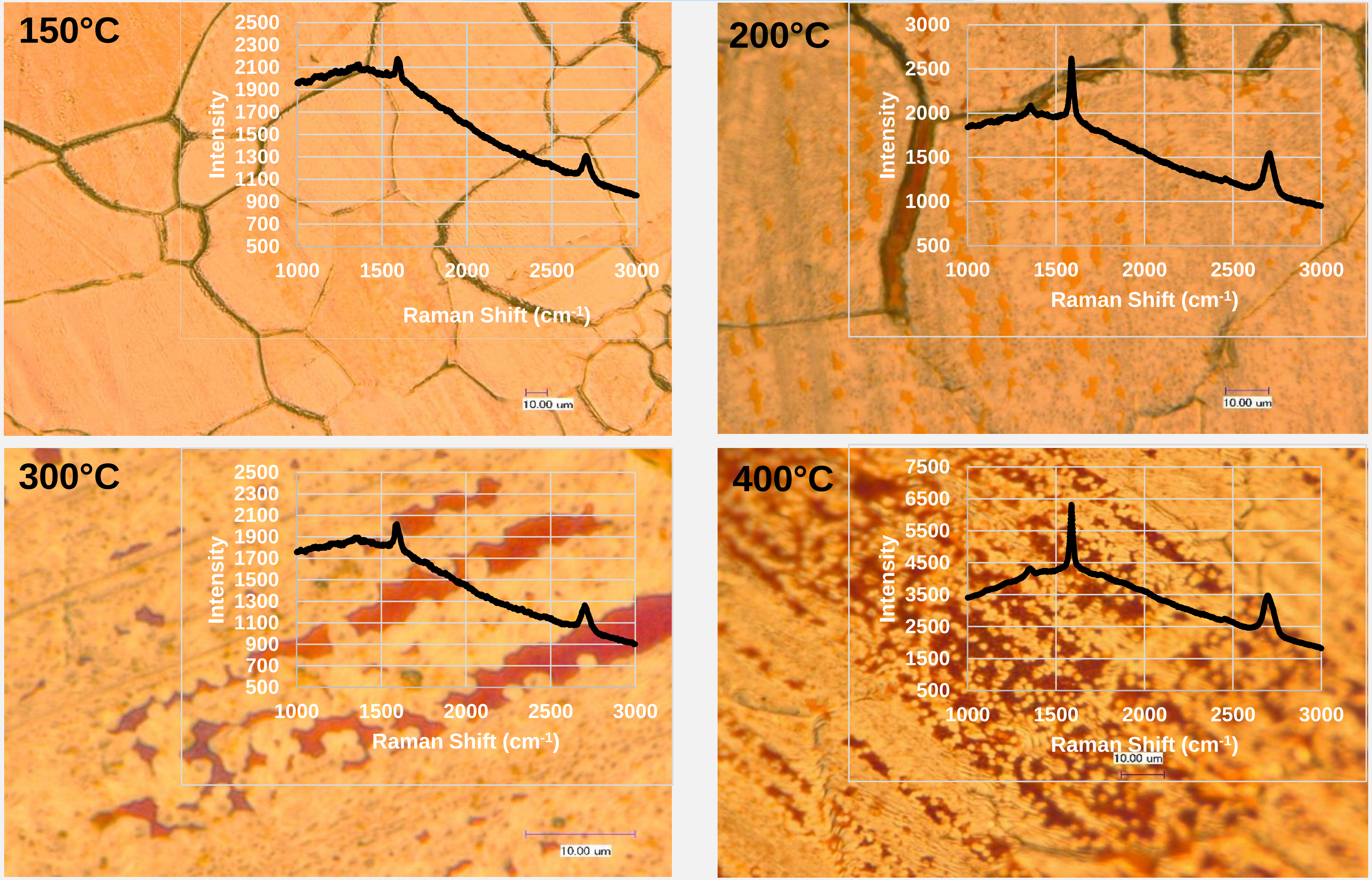
1. We can grow graphene directly on polymer materials
2. Less energy required and shorter synthesis time.

So we try to fabricate graphene at low temperature.



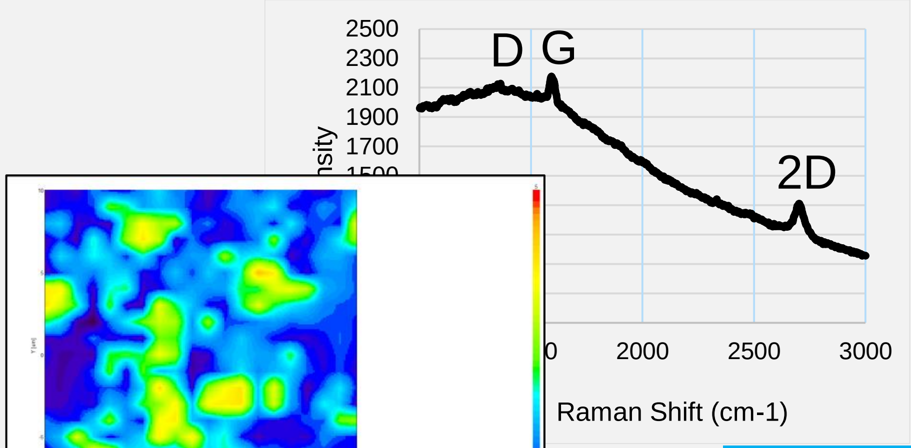
OM Images of Low Temp CVD Graphene Domains

Deposition time : 5 minutes

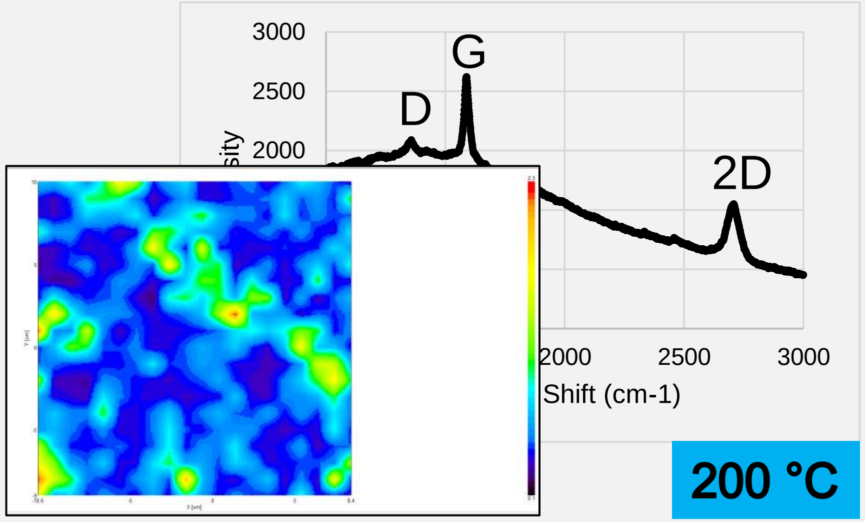


Raman mapping (2D/G) peak

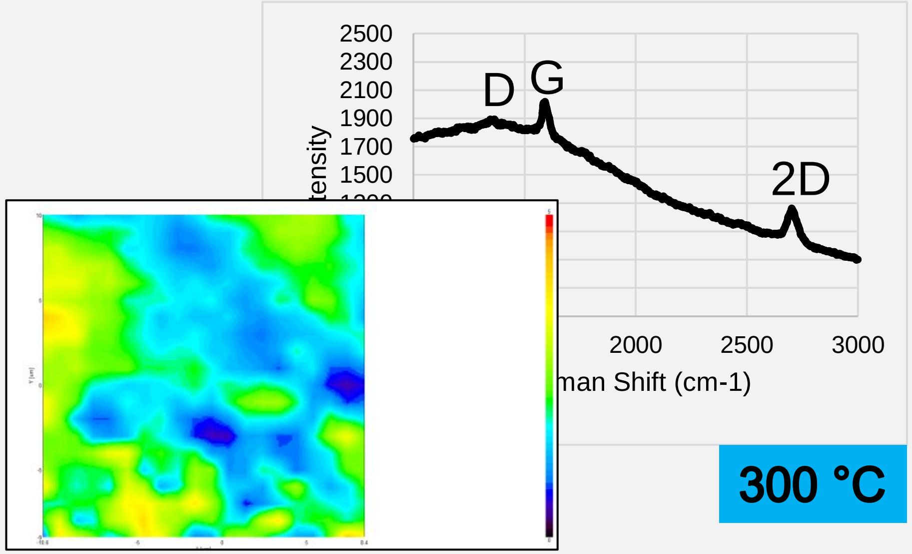
To check concentration and distribution of graphene layers



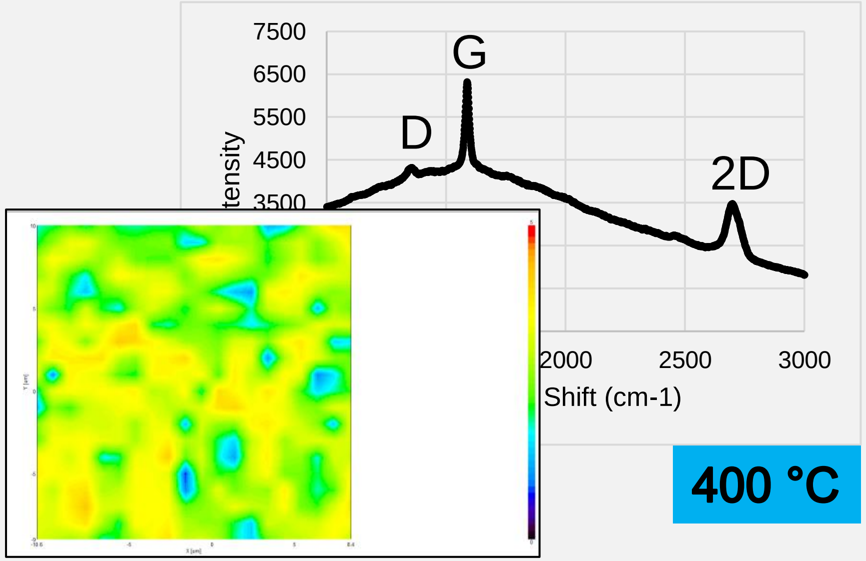
150 °C



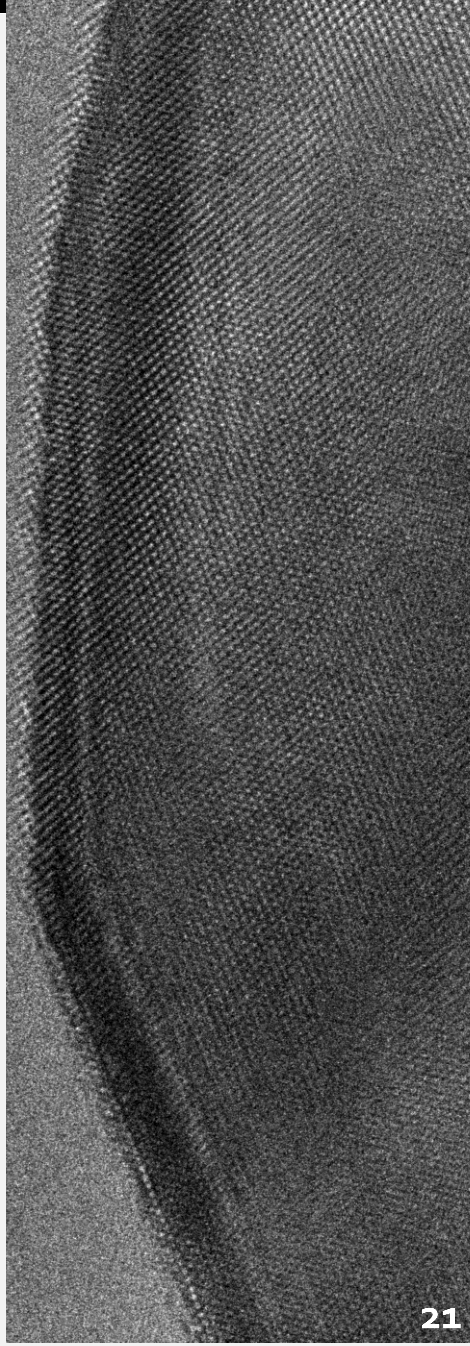
200 °C



300 °C

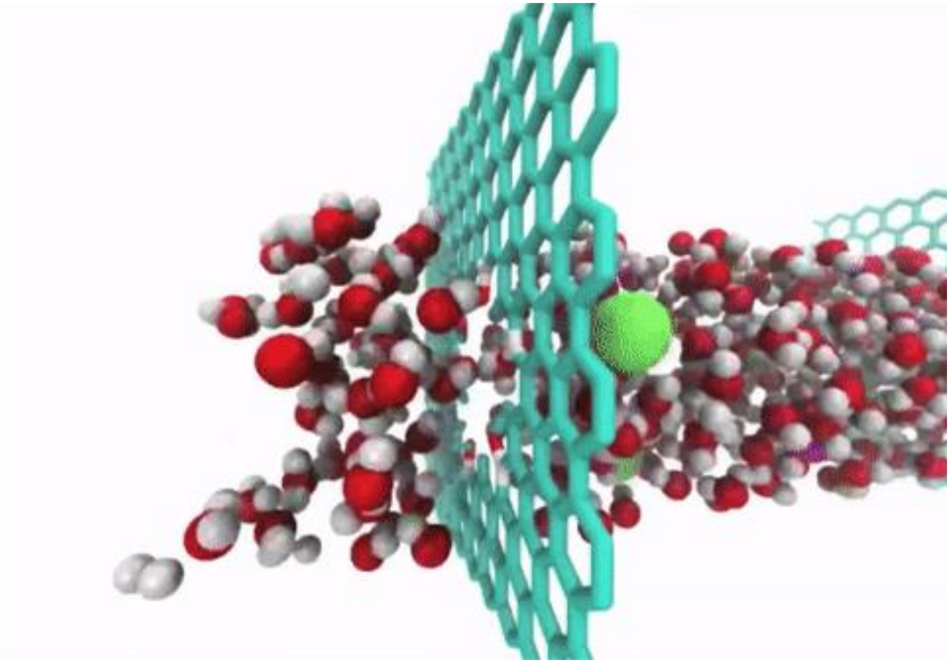


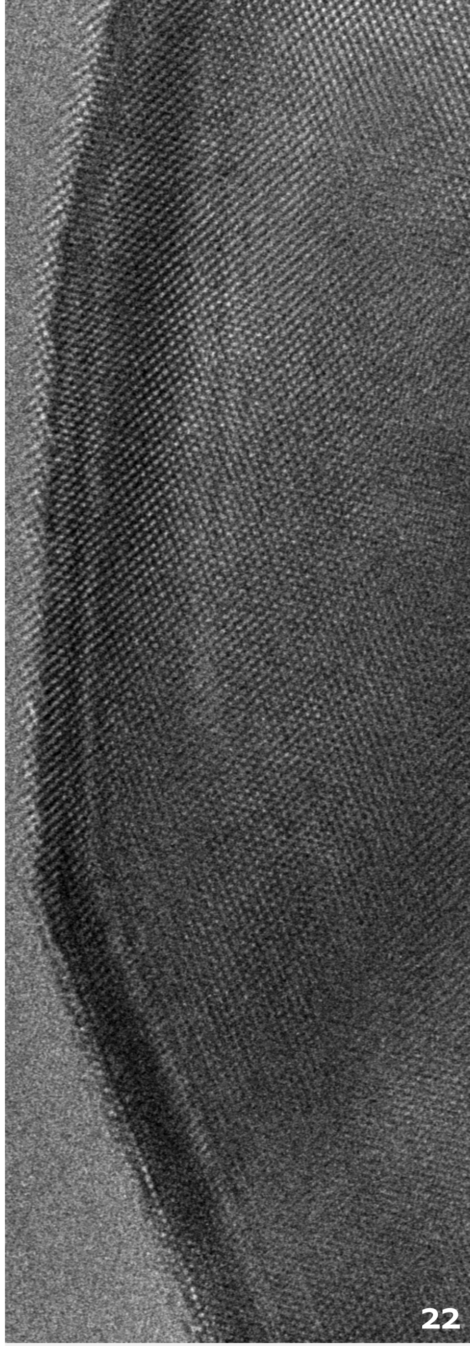
400 °C



NEXT STEP

1. Achieve at least a few millimeters in diameter of continues graphene at low temperature.
2. Direct graphene growth on polymer substrates.
3. Fabrication of nanoporous graphene using hydrogen etching technique/ion irradiation.





UTM
UNIVERSITI TEKNOLOGI MALAYSIA

AMTEC
Advanced Membrane Technology Research Centre

MyMembrane
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THANK YOU

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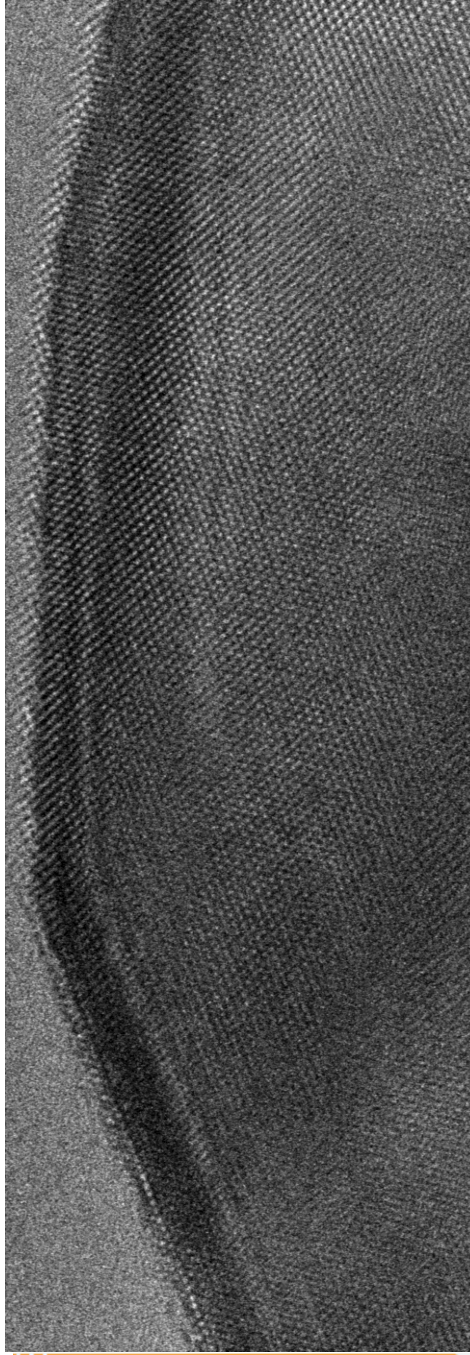


MALAYSIA MEMBRANE SOCIETY

METHODOLOGY

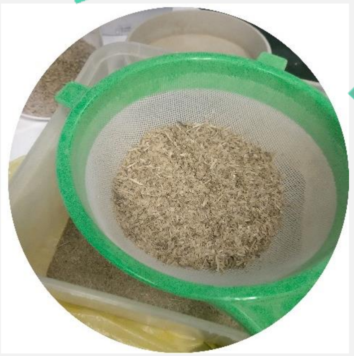
Preparation of Precursors

Rice husk →→→Rice Husk Powder

Raw Rice Husk

Weigh

Grind



Sift

Rice Husk Powder

METHODOLOGY

1(a): Combustion Process

- 10 grams of rice husk powder in crucible were burnt in furnace **to get rice husk ash (RHA)** —the carbon source in this method.
- The rice husk ash (RHA) produced is less than 10 grams.
- The holding time for the combustion process is **2 hours.**

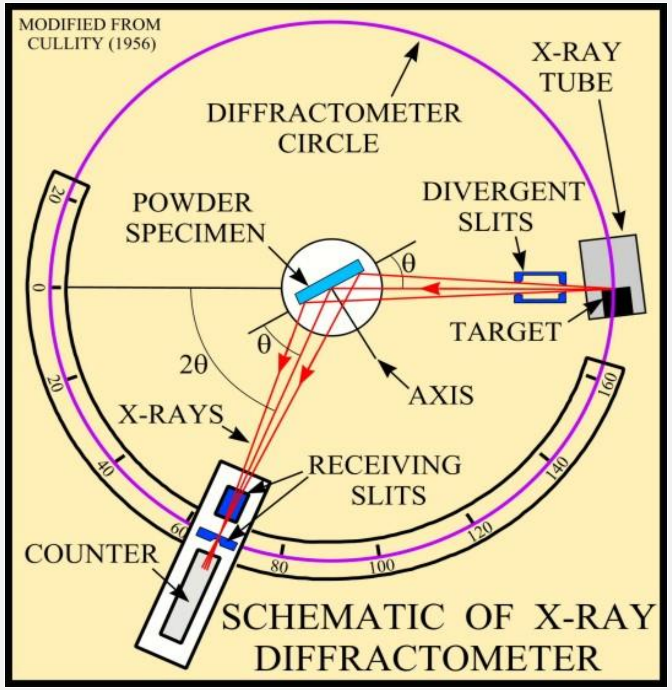
MANIPULATED VARIABLES:

Combustion Temperature (300 ℃, 350 ℃, 400 ℃, 450℃ and 500℃)

METHODOLOGY

1(b): Analysis on RHA

(i) X-Ray Diffraction Analysis (XRD)

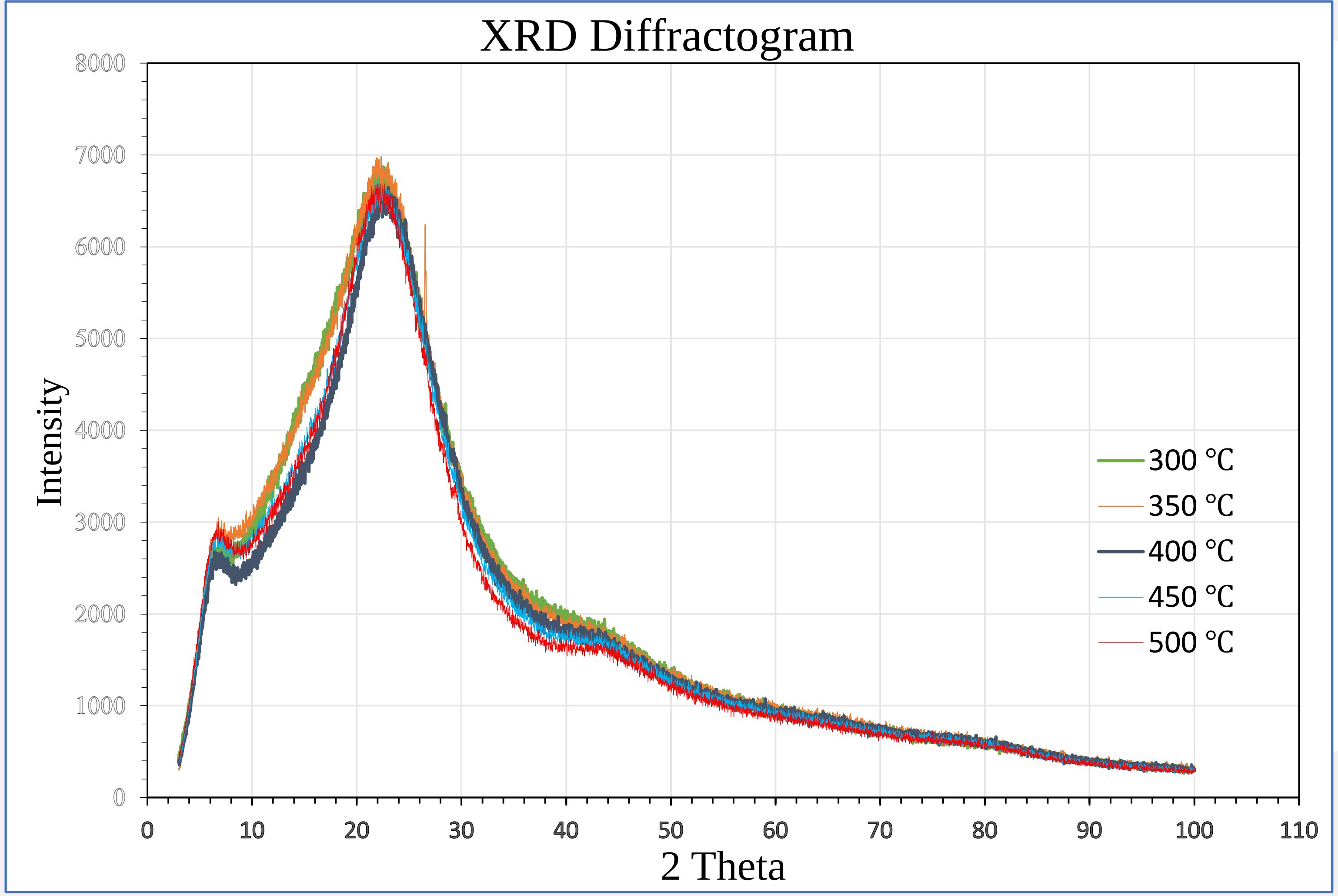


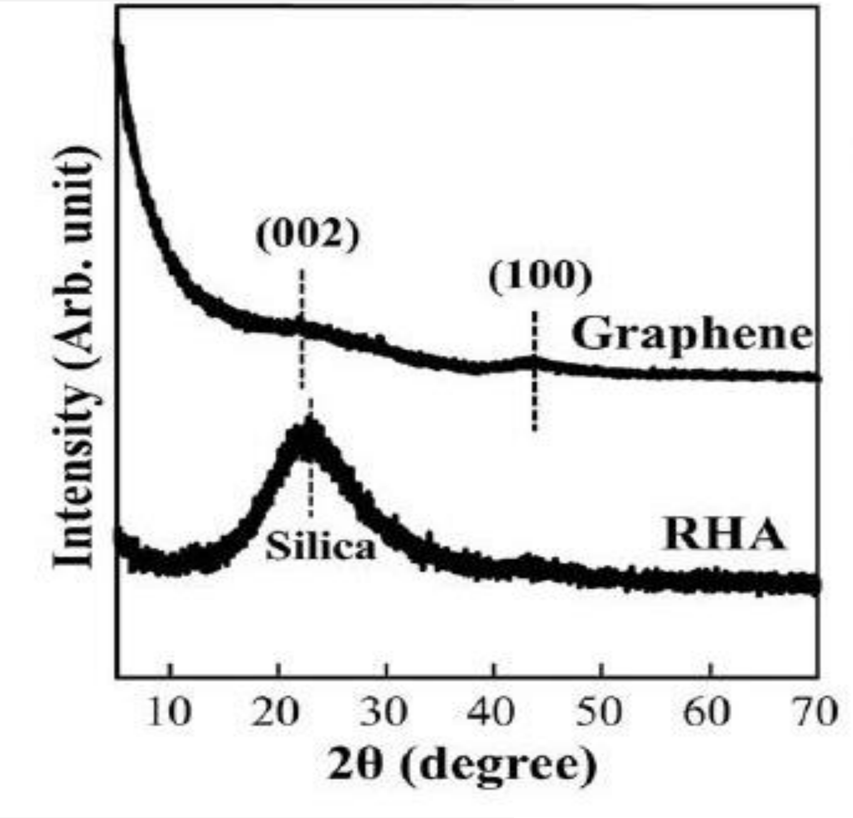
Schematic of X-Ray Diffractometer.
(Crain's Petrophysical Handbook, 2015)

- The crystal structure of the RHA was determined via XRD analysis.
- The interaction of the incident rays with the sample produces a diffracted ray when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$).
- These diffracted rays are counted by detector and analyzed with the help of software in computer.

RESULTS

XRD Results of RHA

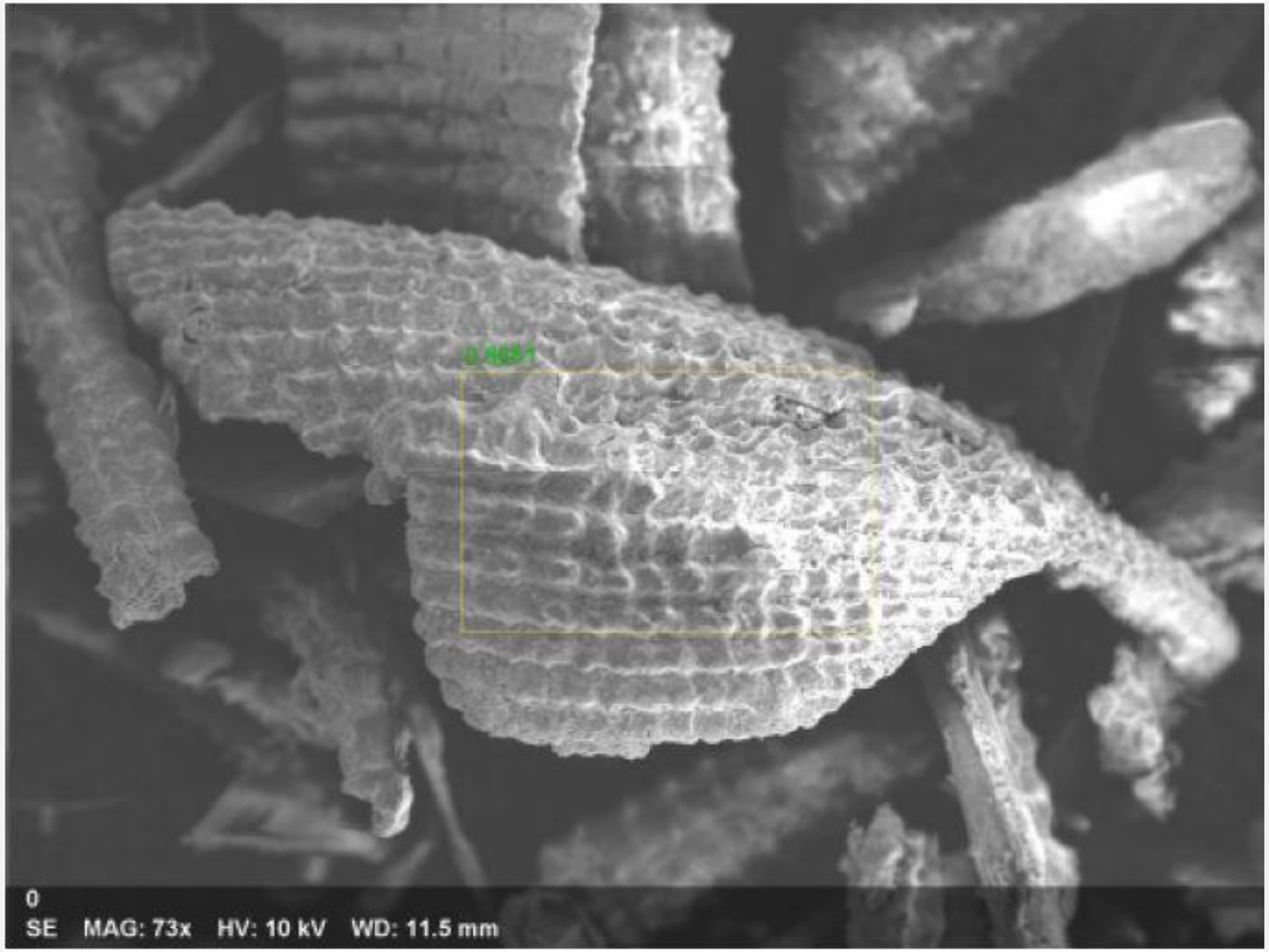




X-Ray diffraction patterns of RHA (Muramatsu *et al.*, 2014)

RESULTS

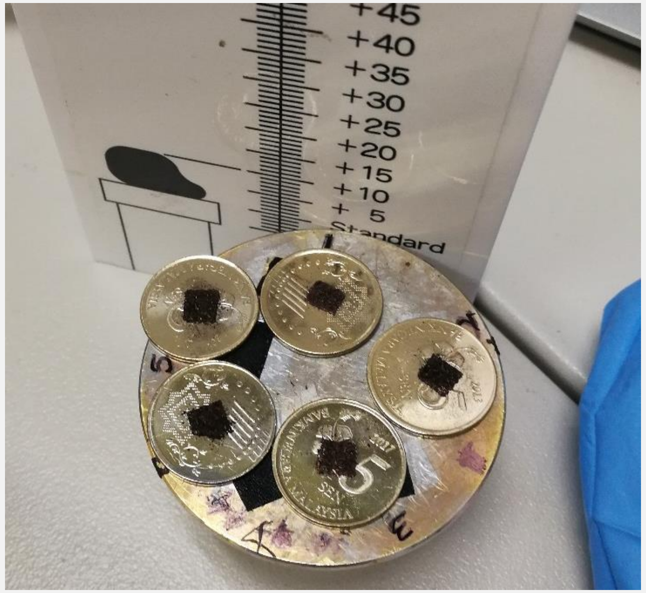
Variable-Pressure Scanning Electron Microscopy (VPSEM) Image of RHA



METHODOLOGY

1(b): Analysis on RHA

(ii) Energy Dispersive X-Ray Analysis (EDX)

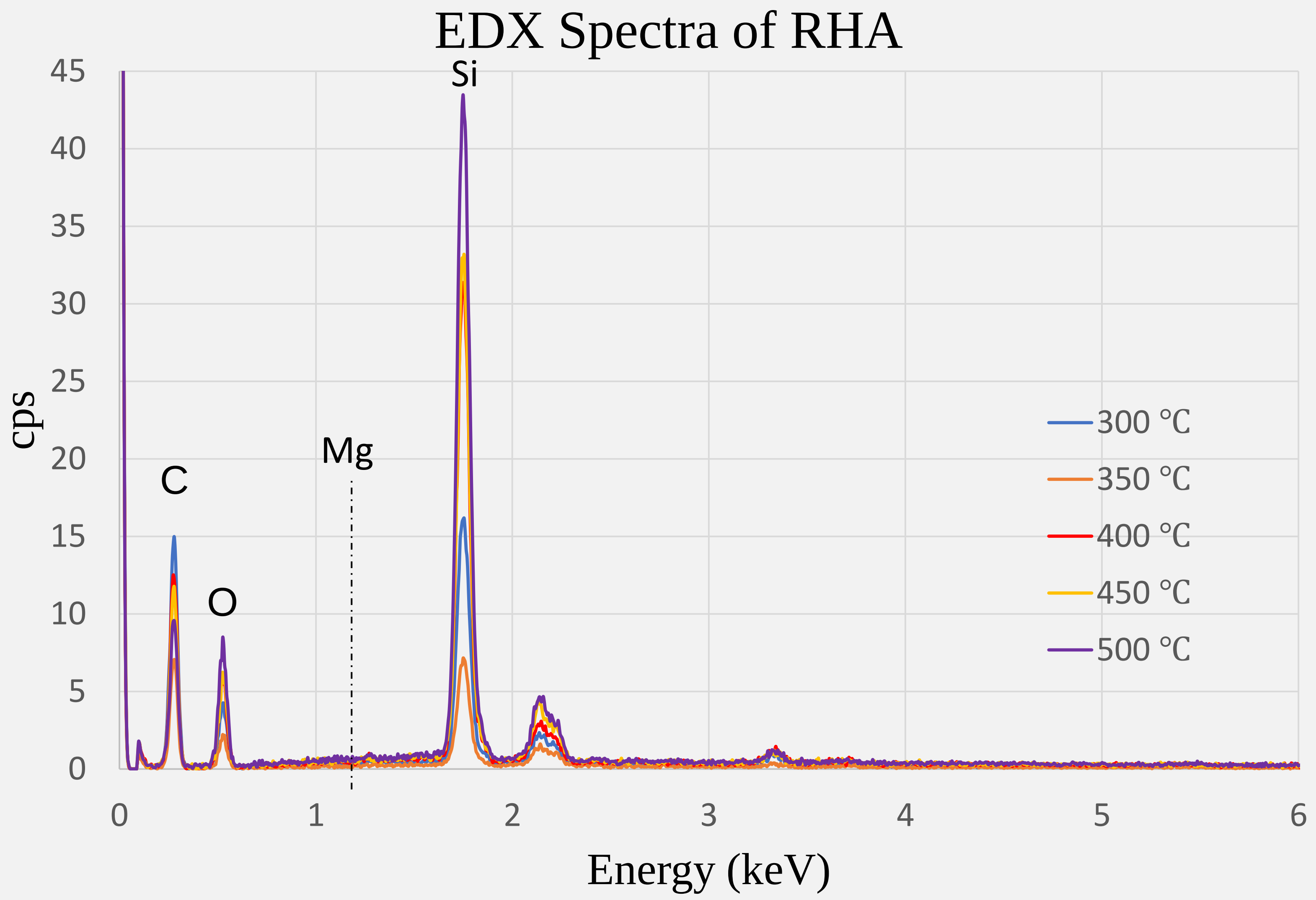


- EDX allows elemental composition of the RHA to be known by measuring the energies of the X-Rays emitted by RHA after exciting by electron beams.

- The emitted X-Rays are the characteristic of the energy difference between the two shells and of the atomic structure of the emitting element.

RESULTS

EDX Results of RHA



RESULTS

EDX Results of RHA

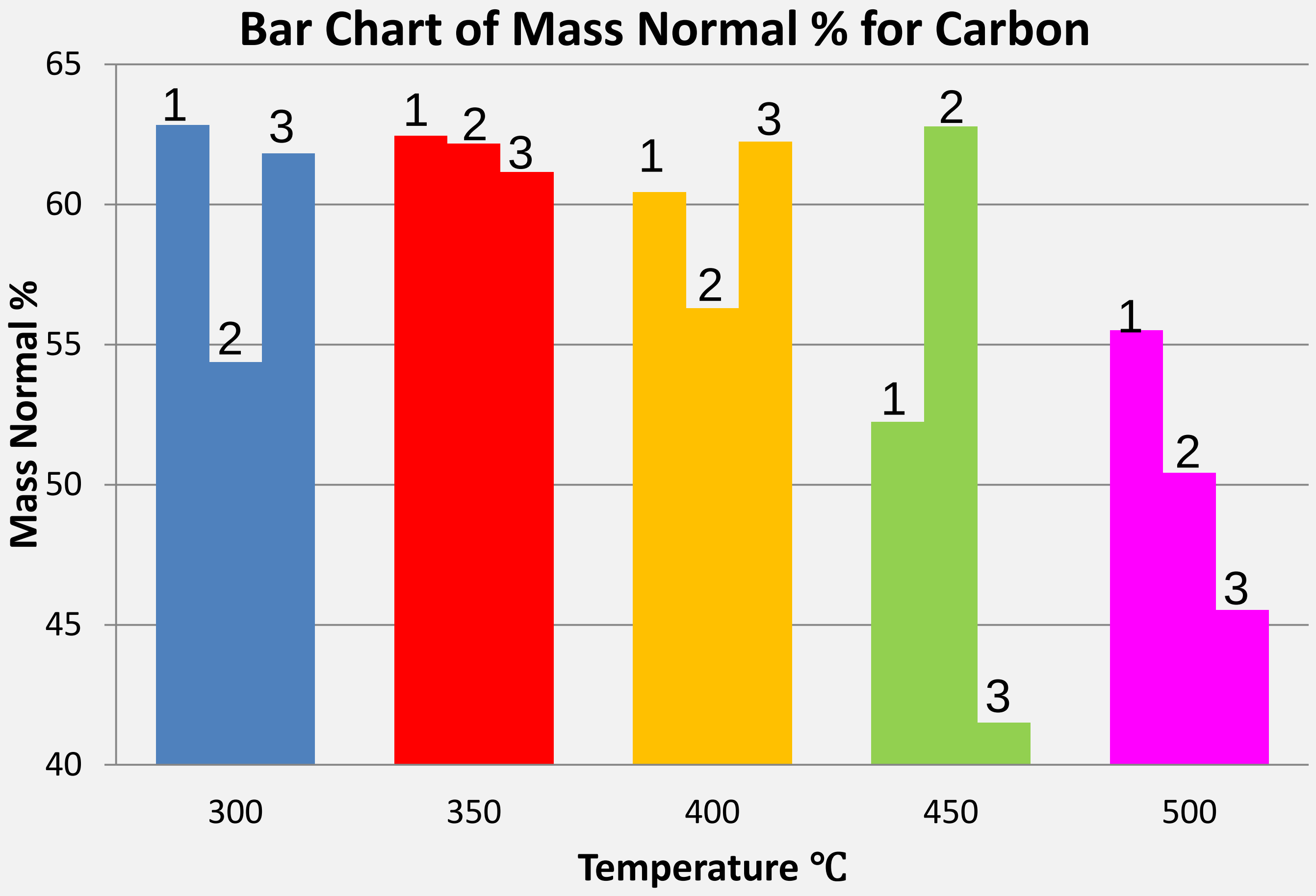


Table 1: Average Mass Normal % of Element

	Average Mass Normal % of Element			
Temperature °C	C	O	Si	Mg
300	59.67	21.66	17.74	0.92
350	61.93	23.15	14.67	0.25
400	59.66	20.93	18.52	0.89
450	52.18	25.8	21.59	0.43
500	50.49	25.86	22.75	0.93

RESULTS OF COMBUSTION PROCESS

First and second objectives which are

1. To analyze the composition of RHA in the combustion process at different elevated temperatures.
2. To determine the optimum combustion temperature of rice husk for highest percentage of carbon composition.

have been **achieved.**

The optimum combustion temperature of rice husk for highest percentage of carbon composition is 350 °C. Thus, rice husk ash produced at 350 °C was used in the following activation process to synthesize graphene.

This is different from the temperature applied by (Rhee *et al.*, 2015) who thermal treated rice husk at the range of 500°C to 700°C to synthesized graphene.

METHODOLOGY

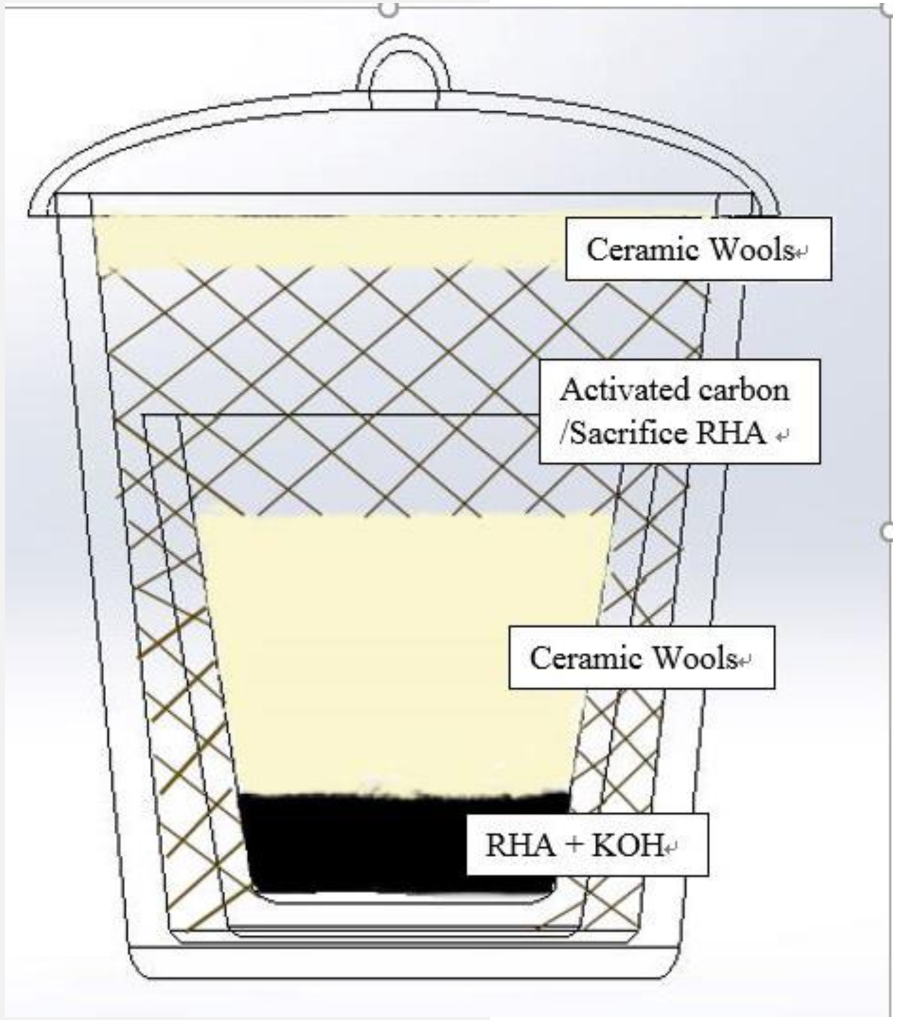
2. Activated Carbon Process

- This figure shows the setup of the sample for activation
- Ceramic wools was used to prevent oxidation of sample.
- Activated carbon was used to improve the reaction between RHA and KOH and also to reduce the oxidation of sample.

MANIPULATED VARIABLES

Impregnation ratio (RHA : KOH)

(1:1, 1:3 and 1: 5)



STEPS

1.

2.

3.

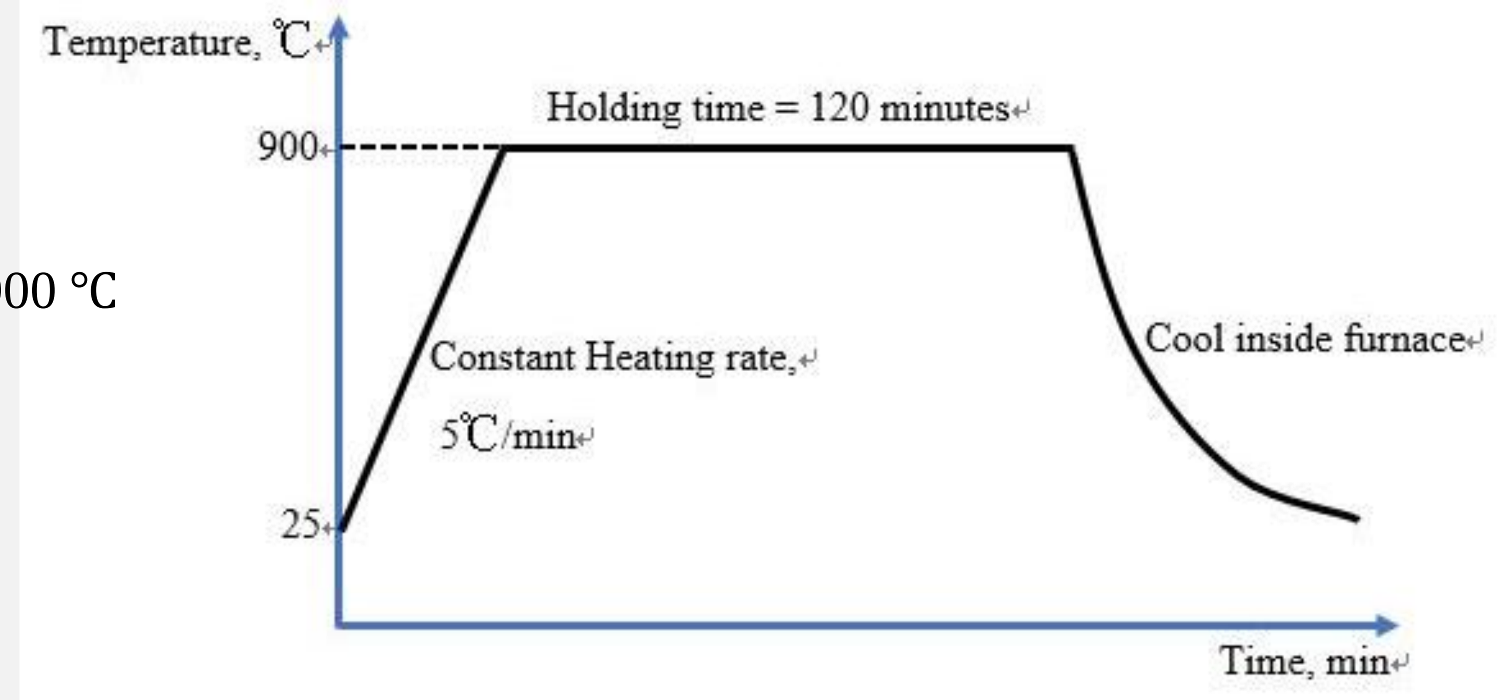
4.

Furnace

Activation temperature : 900 ℃

Holding time : 2 hours

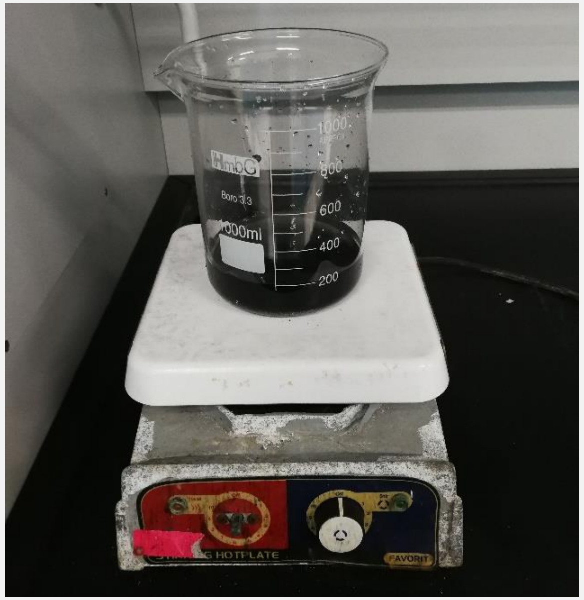
(Singh, P. *et al.*, 2017)



METHODOLOGY

3. Washing Process (ASTM G131 Standard Practice for Cleaning of Materials and Component by Ultrasonic Techniques)

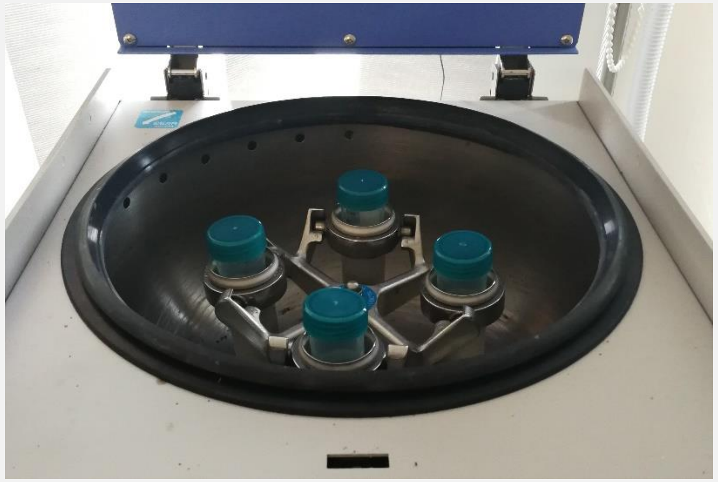
1. The activated sample is removed from the crucible.



2. Activated sample was put into a distilled water containing beaker and stirred for 30 minutes.

METHODOLOGY

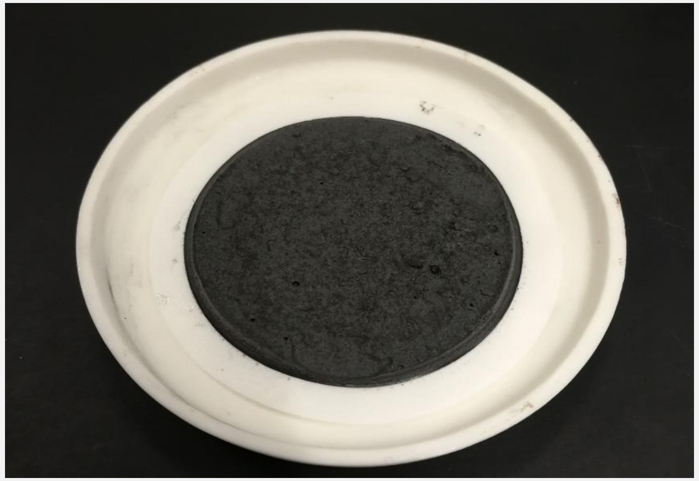
3. Washing Process—(continue)



3. Centrifuging Process

4. Sonicating process

5. Filter



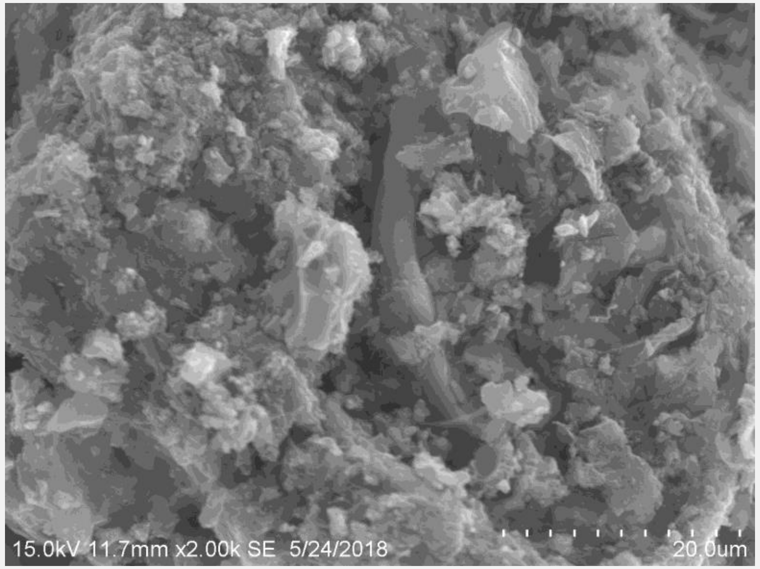
6. Drying

RESULTS

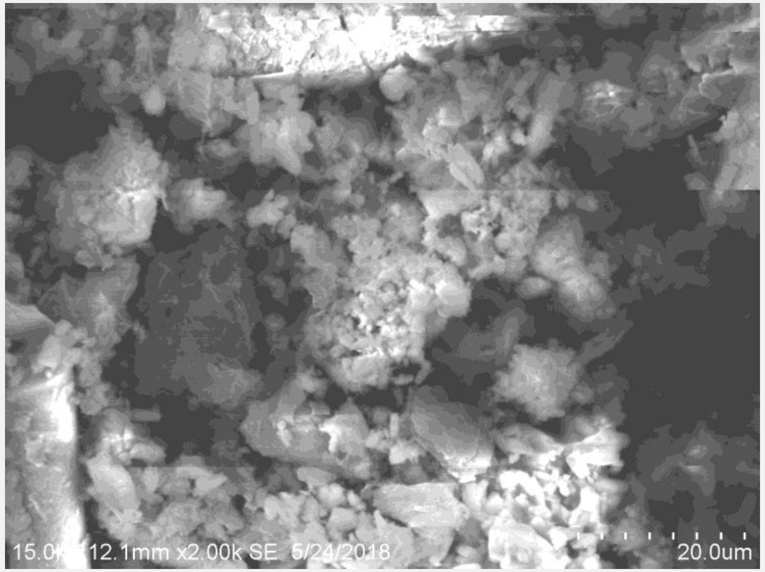
Analysis of RHA-Derived Graphene (RGRAH)

(i) Variable-Pressure Scanning Electron Microscopy Image of RGRAH Produced

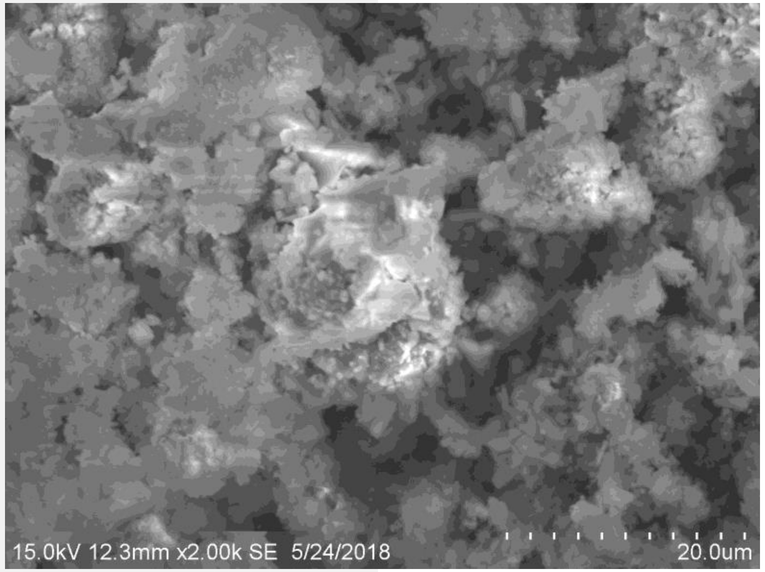
1:1



1:3



1:5



RESULTS

Analysis of RHA-Derived Graphene (RGRAH)

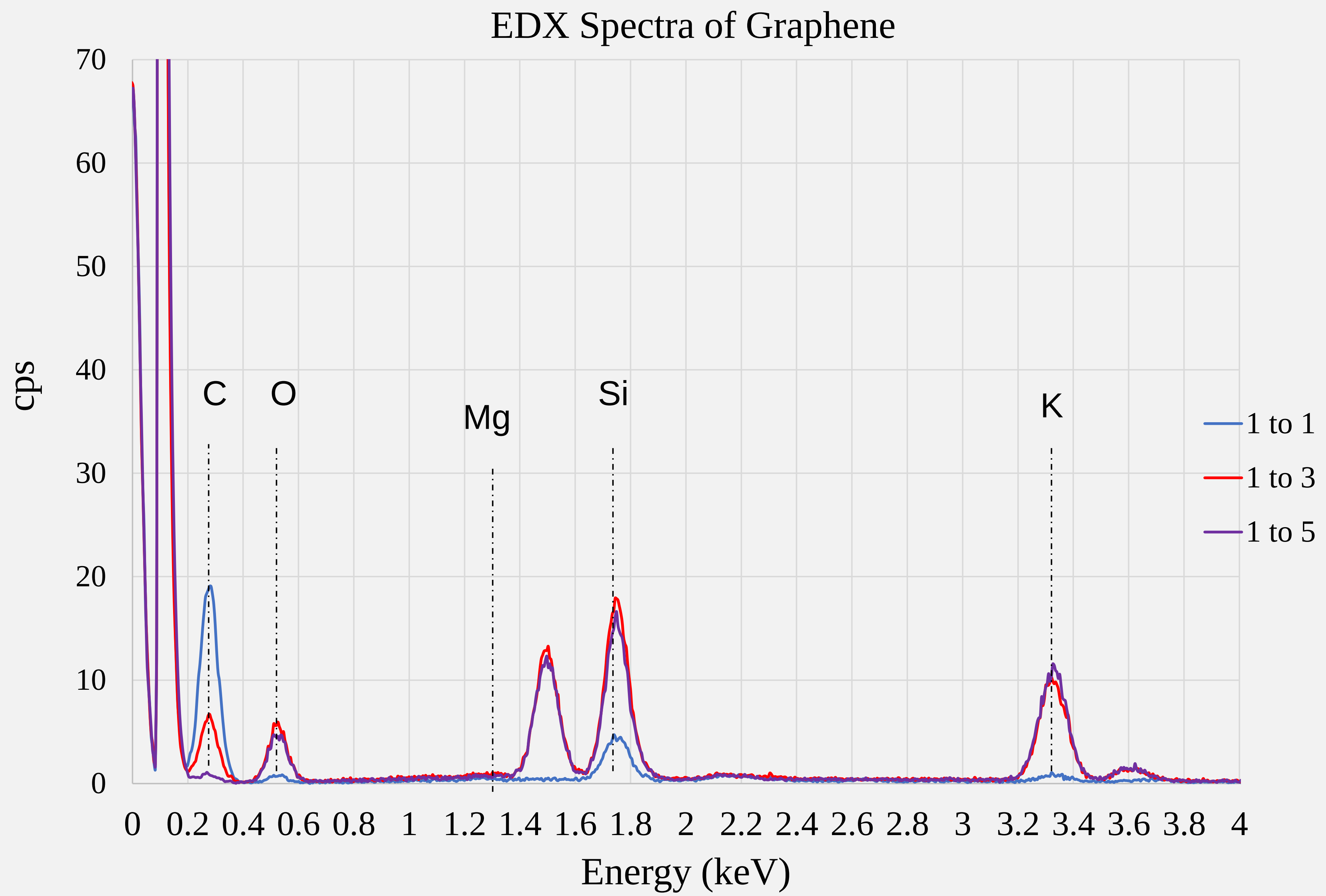
(ii) Energy Dispersive X-Ray Analysis (EDX):

Same as the EDX analysis on the RHA, activated RHA was analyzed to compare the composition of the samples activated by different amount of KOH.

Table 2: Mass Normal % of Element in Graphene

Impregnation ratio	Mass Normal % of Element in Graphene				
	C	O	Si	Mg	K
1:1	82.76	6.34	7.36	0.62	2.91
1:3	25.36	32.76	14.15	0.13	27.59
1:5	5.7	38.15	17.6	0.41	40.85

- The carbon composition decreased with the increase of the amount of KOH.
- The silicon, oxygen and potassium composition increased with the increase of the amount of KOH.

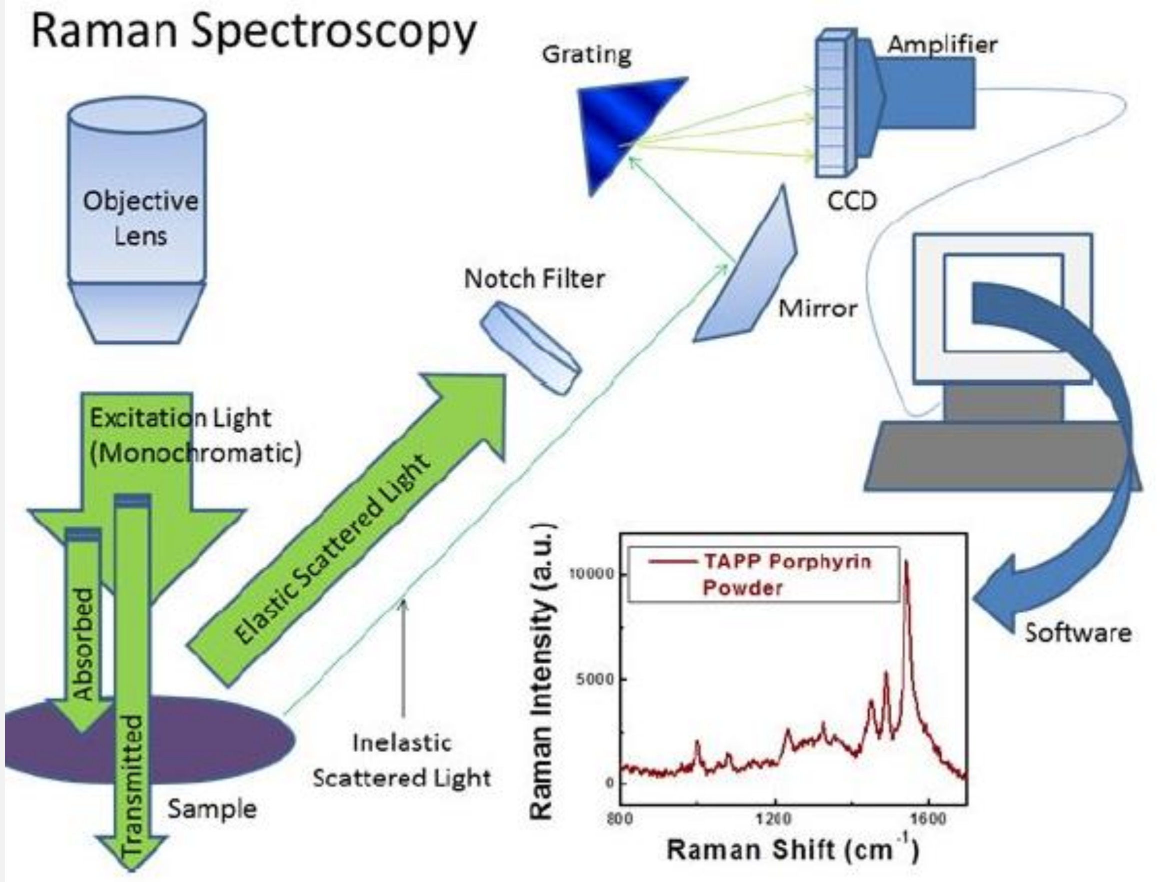


EDX Spectra of Graphene
cps
Energy (keV)
C
O
Mg
Si
K
1 to 1
1 to 3
1 to 5
0
10
20
30
40
50
60
70
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2 2.2 2.4 2.6 2.8 3 3.2 3.4 3.6 3.8 4

METHODOLOGY

Analysis of Analysis of RHA-Derived Graphene (RGRAH)

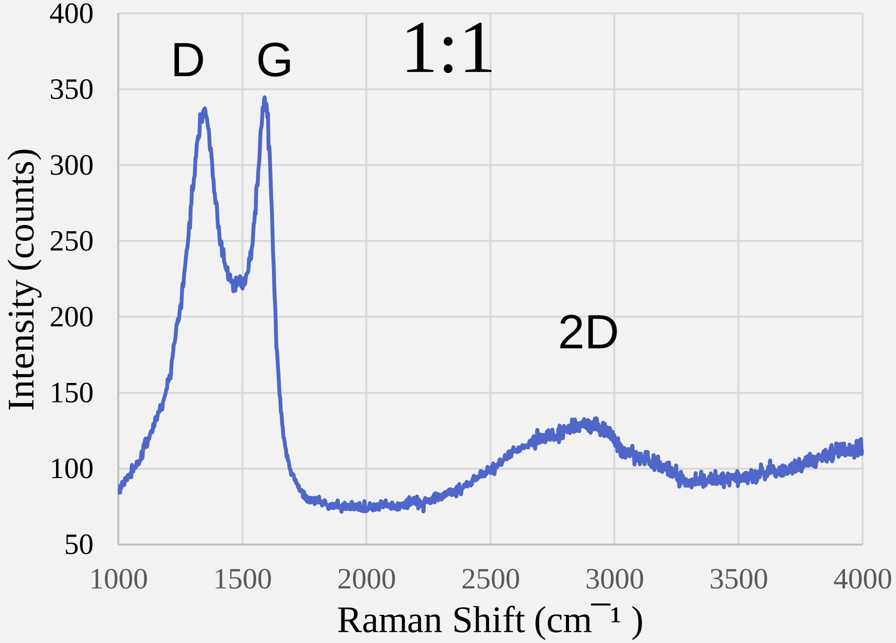
(ii) Raman Spectroscopy Analysis:

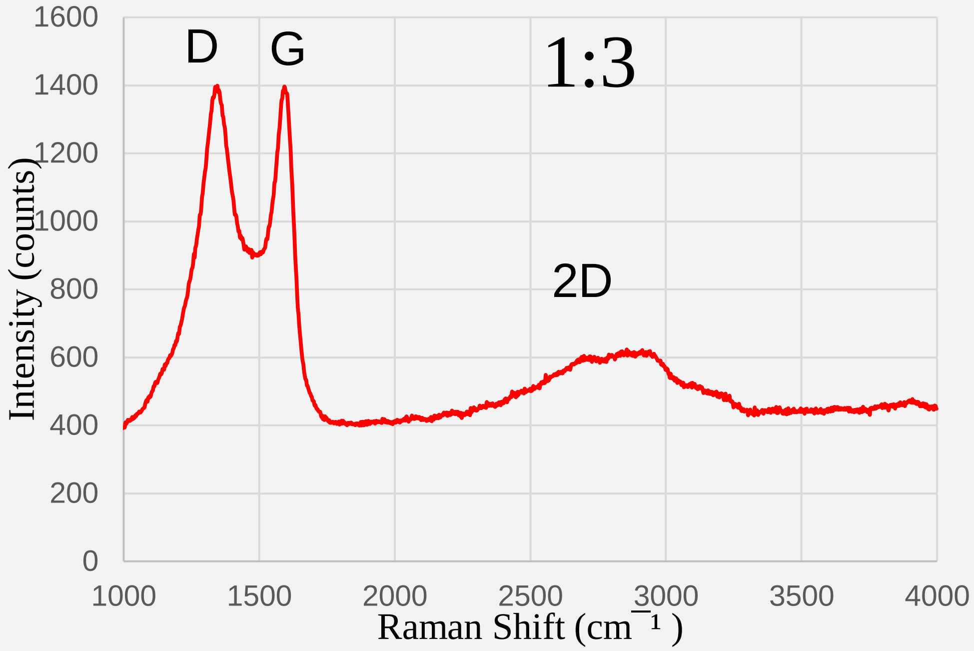


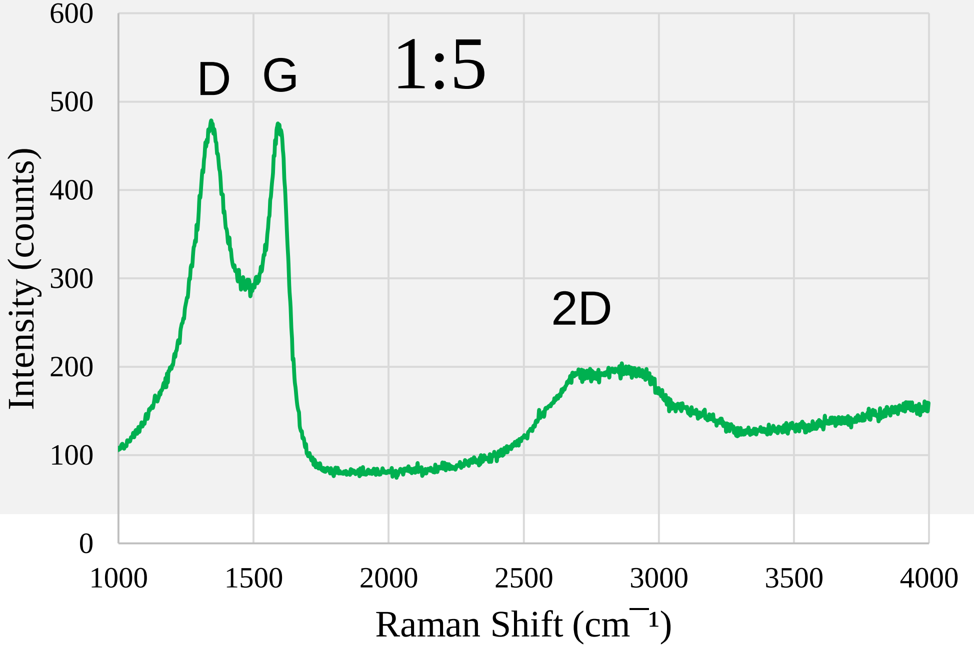
Schematic Drawing of Raman Spectroscopy.
(Halvorson *et al.*, 2010)

- The wavelength and intensity of inelastic scattered light from molecules are measured
- The sample was illuminated with a monochromatic laser beam and scattered light arise after there is an inelastic collision between the incident beam and the molecules of the sample
- Scattered light that has different frequency with the incident beam is used to construct a Raman spectrum

Raman Spectra of RGRAH Produced





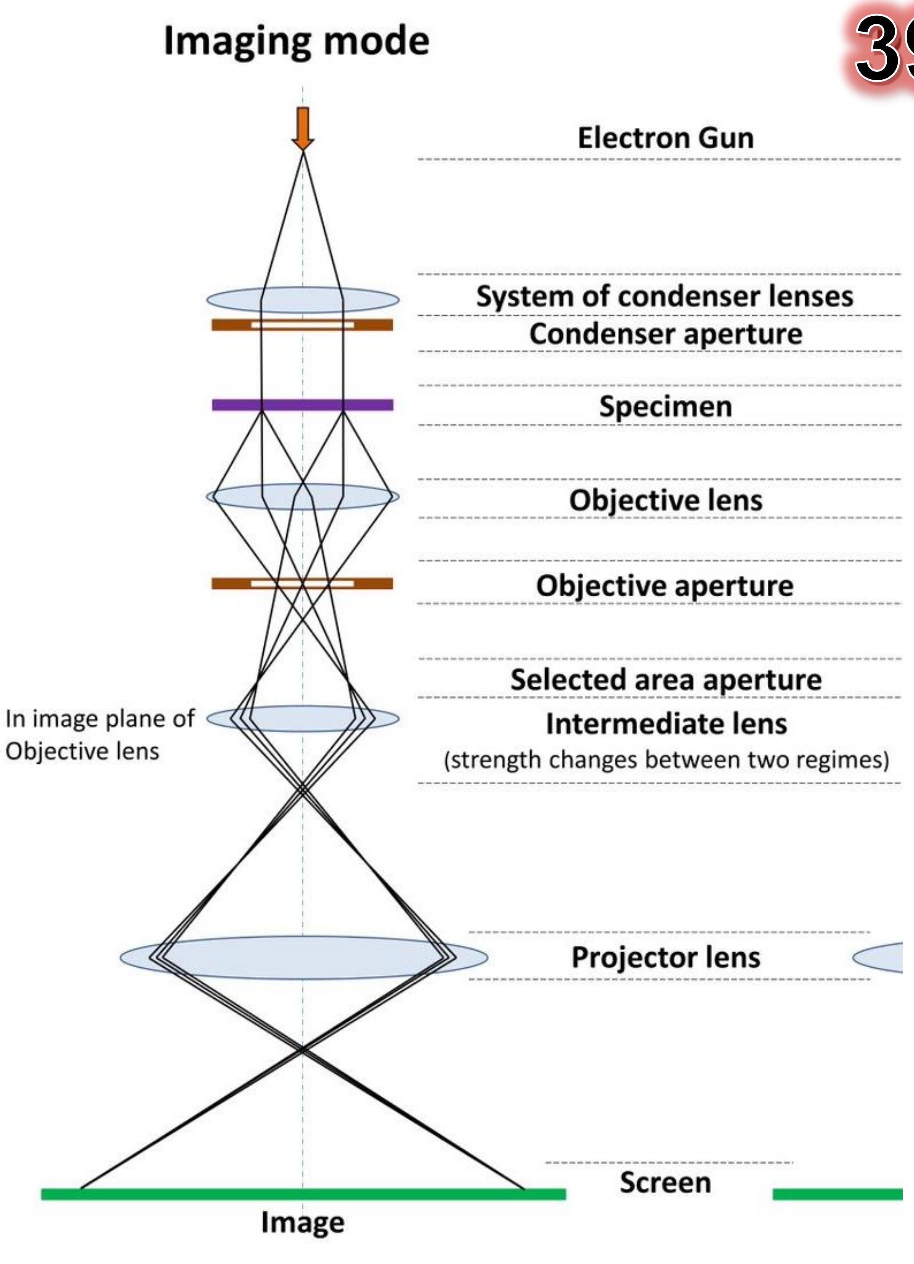


METHODOLOGY

Analysis of RHA-Derived Graphene (RGRAH)

(iii) Transmission Electron Microscopy Analysis:

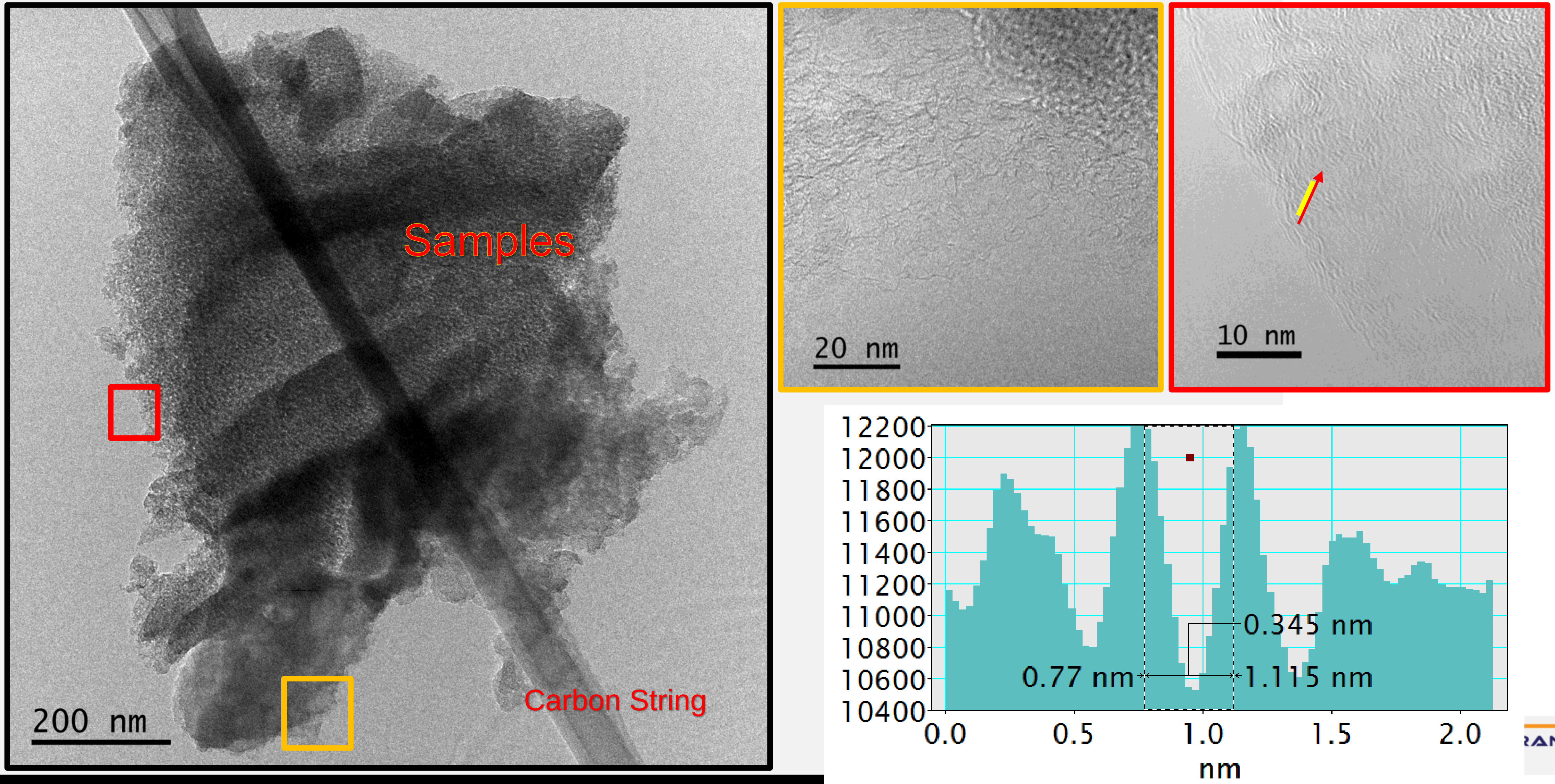
- Electron beam is transmitted through a specimen to form an image.
- Image formed from the interaction of the electrons with the samples
- The image is then magnified and focused onto an imaging device.



RESULTS

(iii) Transmission Electron Microscopy Image

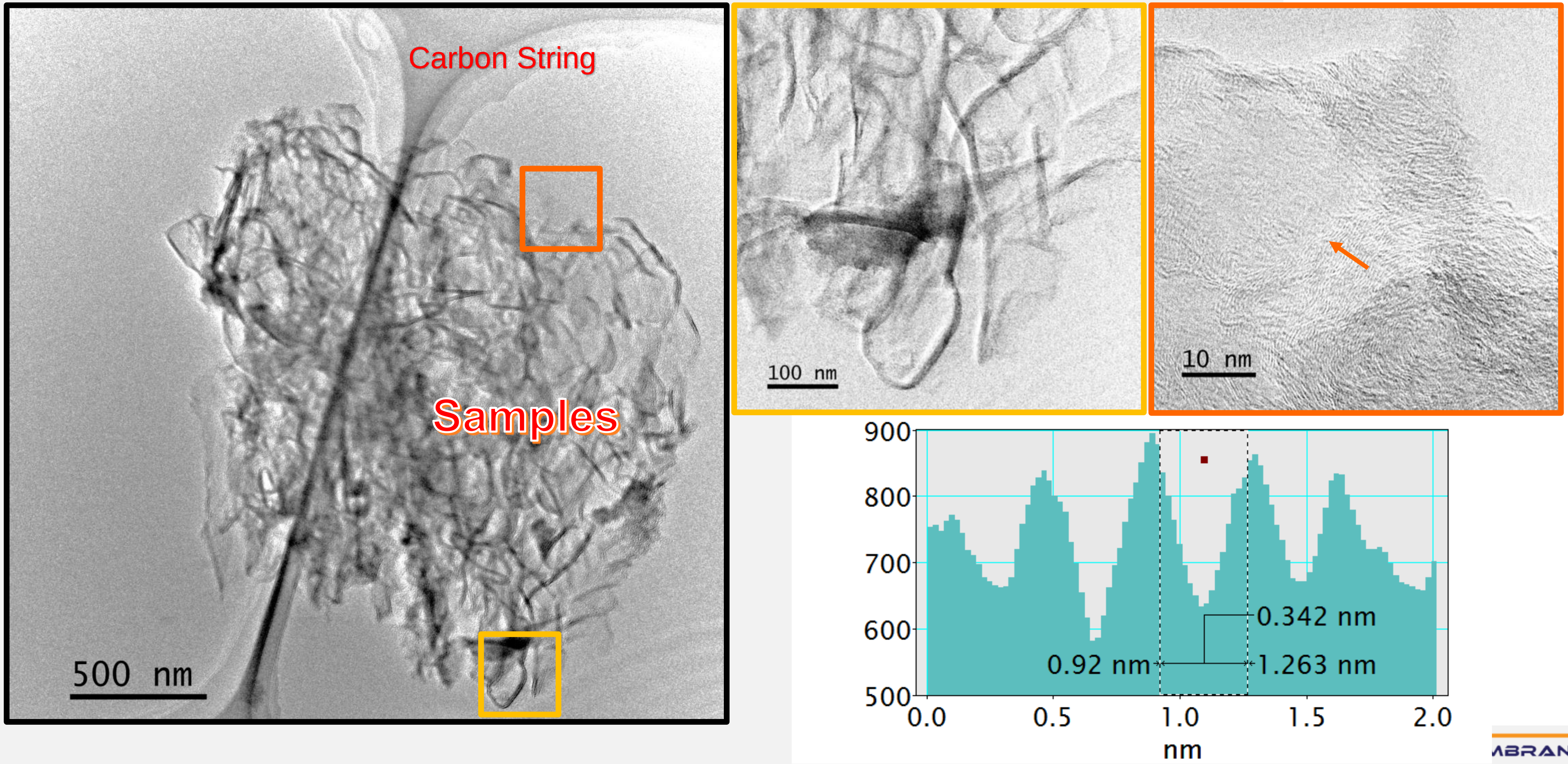
(a) RHA : KOH = 1: 1



RESULTS

(iii) Transmission Electron Microscopy Image

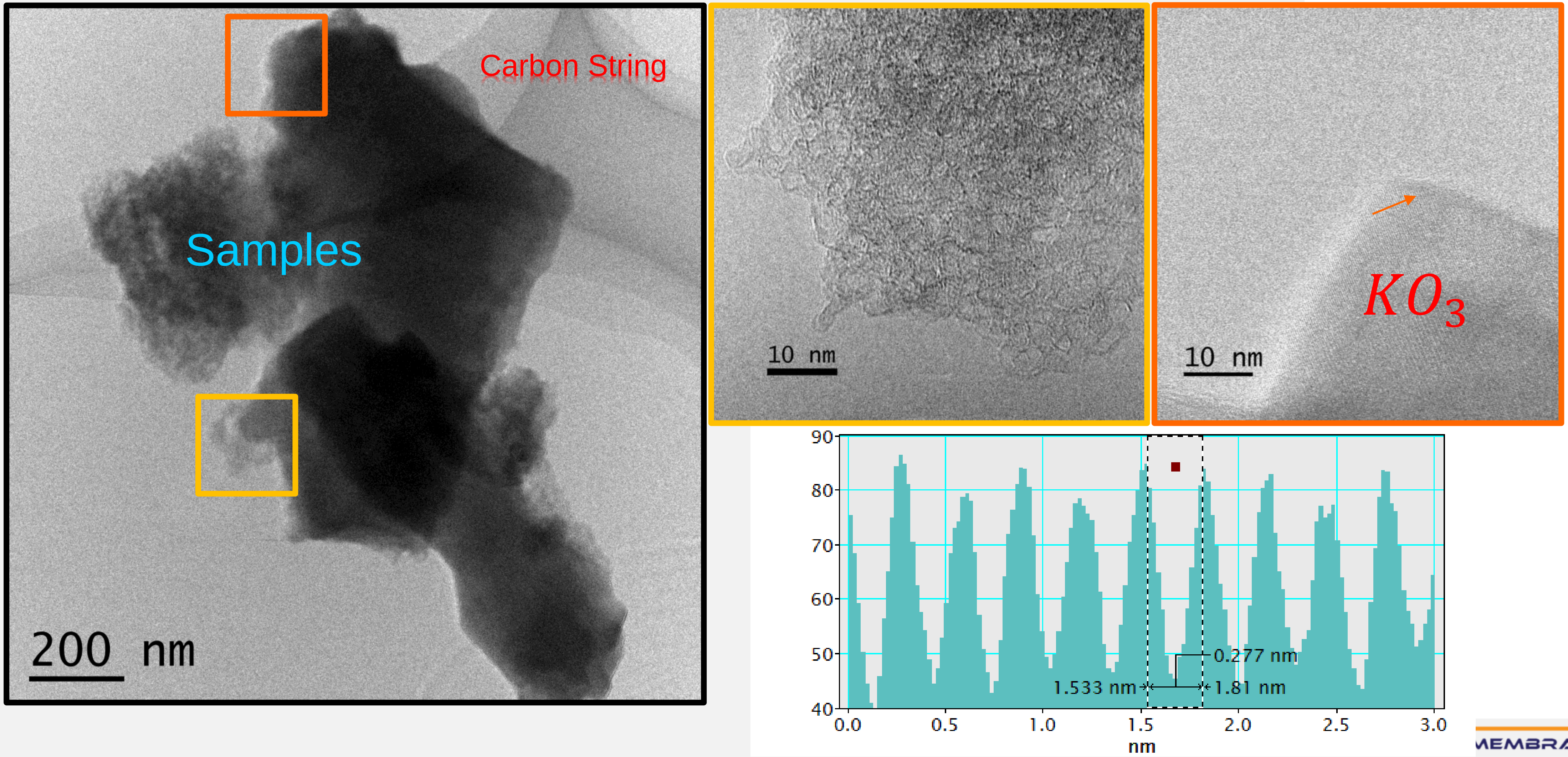
(b) RHA : KOH = 1: 3



RESULTS

(iii) Transmission Electron Microscopy Image

(c) RHA : KOH = 1: 5



JCPDS Database

77–1270 | Wavelength= 1.54060 | C

KO3

Potassium Ozonide

Rad.: CuKa1 λ: 1.54060 Filter: d–sp: Calculated

Cut off: 17.7 Int.: Calculated I/Icor.: 4.80

Ref: Calculated from ICSD using POWD–12++, (1997)

Ref: Jansen, M., Schnick, W., Angew. Chem., 97, 48 (1985)

Sys.: Tetragonal S.G.: I4/mcm (140)

a: 8.648(12) b: c: 7.164(14) A: C: 0.8284

α: β: γ: Z: 8 mp:

Ref: Ibid.

Dx: 2.159 Dm: ICSD # : 047163

Peak height intensity. R–factor: 0.063. K O3 type. PSC: tI32.
Mwt: 87.10. Volume[CD]: 535.78.

d(A)	Int	h	k	l	d(A)	Int	h	k	l
6.1150	3	1	1	0	1.5670	9	5	2	1
4.324	289	2	0	0	1.5453	25	2	2	4
3.582	211	0	0	2	1.5328	3	5	1	2
3.4032	533	2	1	1	1.5287	18	4	4	0
3.0575	484	2	2	0	1.4982	2	3	1	4
2.7584	999*	2	0	2	1.4831	5	5	3	0
2.3255	1	2	2	2	1.4413	1	6	0	0
2.2744	97	3	2	1	1.4060	1	4	4	2
2.1620	190	4	0	0	1.4007	3	4	3	3
2.0383	8	3	3	0	1.3945	31	6	1	1
2.0318	50	2	1	3	1.3792	23	4	0	4
2.0129	49	4	1	1	1.3703	5	5	3	2
1.9337	1	4	2	0	1.3673	18	6	2	0
1.8509	7	4	0	2	1.3435	3	2	1	5
1.7910	43	0	0	4	1.3371	24	6	0	2
1.7716	5	3	3	2	1.3272	1	5	4	1
1.7188	1	1	1	4	1.3140	2	4	2	4
1.7016	112	4	2	2	1.2774	1	6	2	2
1.6960	61	5	1	0	1.2687	14	6	3	1
1.6922	20	3	2	3	1.2300	1	3	2	5
1.6812	14	4	3	1	1.2216	9	6	1	3
1.6546	1	2	0	4	1.1992	1	6	4	0
1.5758	8	4	1	3	1.1940	1	0	0	6

RESULTS OF ACTIVATION PROCESS

Third and fourth objectives which are

3. To explicate the effect of impregnation ratio (RHA: KOH) on the characteristics of graphene produced.

4. To characterize the structural and morphological properties of the graphene prepared from activated carbon process.

have been achieved .

- Ratio (RHA:KOH**) 1:1 produced small RGRAH wrinkle**; **1:3 produce larger RGRAH wrinkle** while **1:5 produced mixture of RGRAH wrinkle and oxide layer** (Potassium Ozonide).
- **No flat and straight RGRAH *(no 2D) formed***. There are **defects in the RGRAH** synthesized from this method. *(confirmed by the Raman Spectroscopy results).*
- The **RGRAH flakes formed is wrinkled and contained multilayers**. *(confirmed by the Raman Spectroscopy results).*

CONCLUSION

- **The objectives have been achieved.**
- The **optimum combustion temperature** for higher carbon composition **is 350 ℃. (***EDX analysis results*).
- The **optimum RHA to KOH ratio in this case is 1:3 since the RGRAH found** in this sample is **larger** compared to ratio 1:1. *(TEM analysis results)*
- While **there is metal oxide**—Potassium Ozonide in the RGRAH activated **in the ratio of 1:5 (RHA:KOH)** *(TEM analysis results)*. This result is supported by the EDX results where potassium composition in the third sample is more than 40%.
- The **RHA-derived graphene (RGRAH) formed via activated carbon process is wrinkled and multilayers.** *(TEM image analysis results and Raman Spectroscopy analysis results)*

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