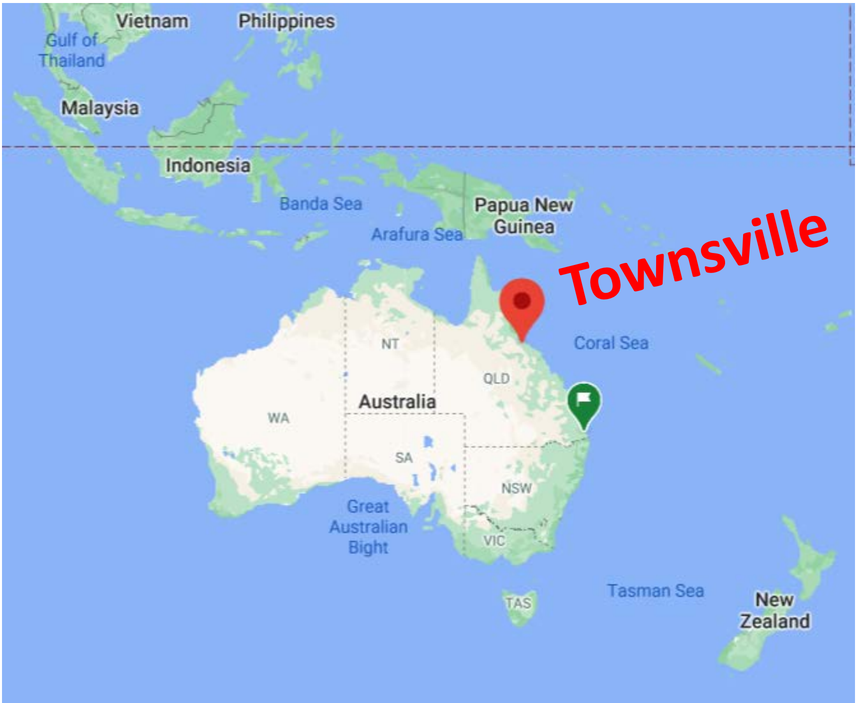
(Microwave and RF) Plasma Enhanced Synthesis of Nanomaterials

Mohan Jacob

College of Science and Engineering
James Cook University
Townsville, Australia



Contributors:

Adeel Zafar
Michael Kamel
Surjith Alancherry
Ahmad Aljumaili
Scarlett Allende

Overview

Plasma Sources (in the context of nanomaterial synthesis)

Microwave Plasma (Downstream Microwave Plasma)

a. Properties
b. Applications

RF Plasma

a. Properties
b. Applications

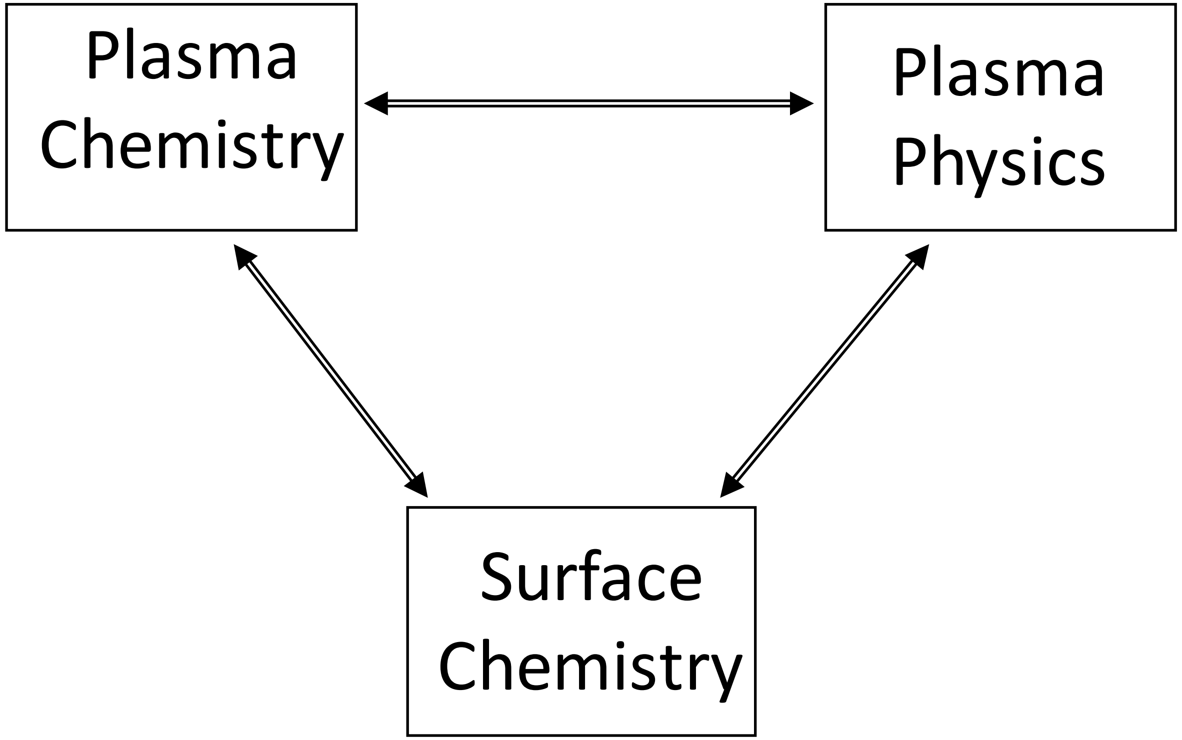
Microwave Assisted Pyrolysis

Conclusions

Plasma processing

Every process using the plasma is a complex interaction between

- gas phase Chemistry
- plasma Physics/conditions
- surface phase Chemistry



Plasma Sources for PECVD and Atmospheric Pressure Plasma

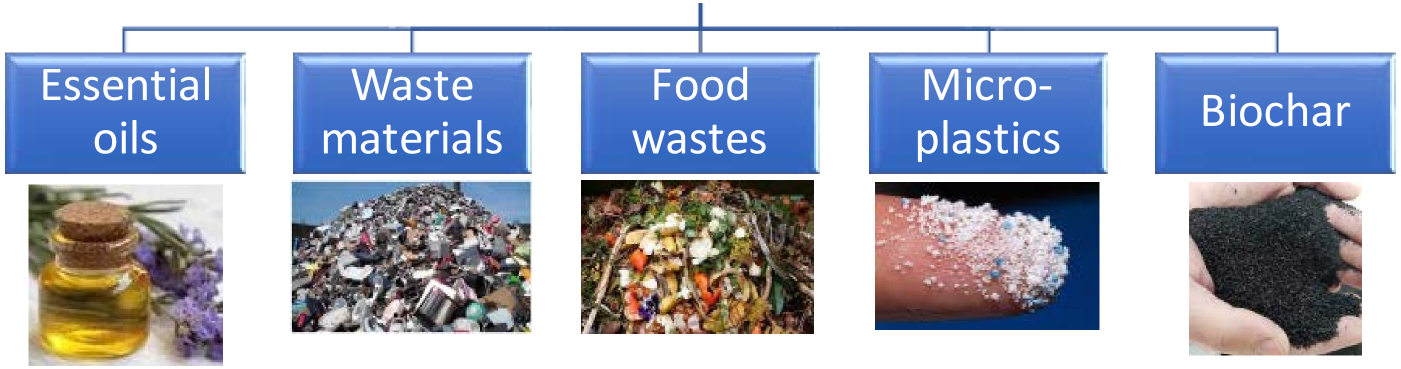
Microwave (~1 - 20 GHz)

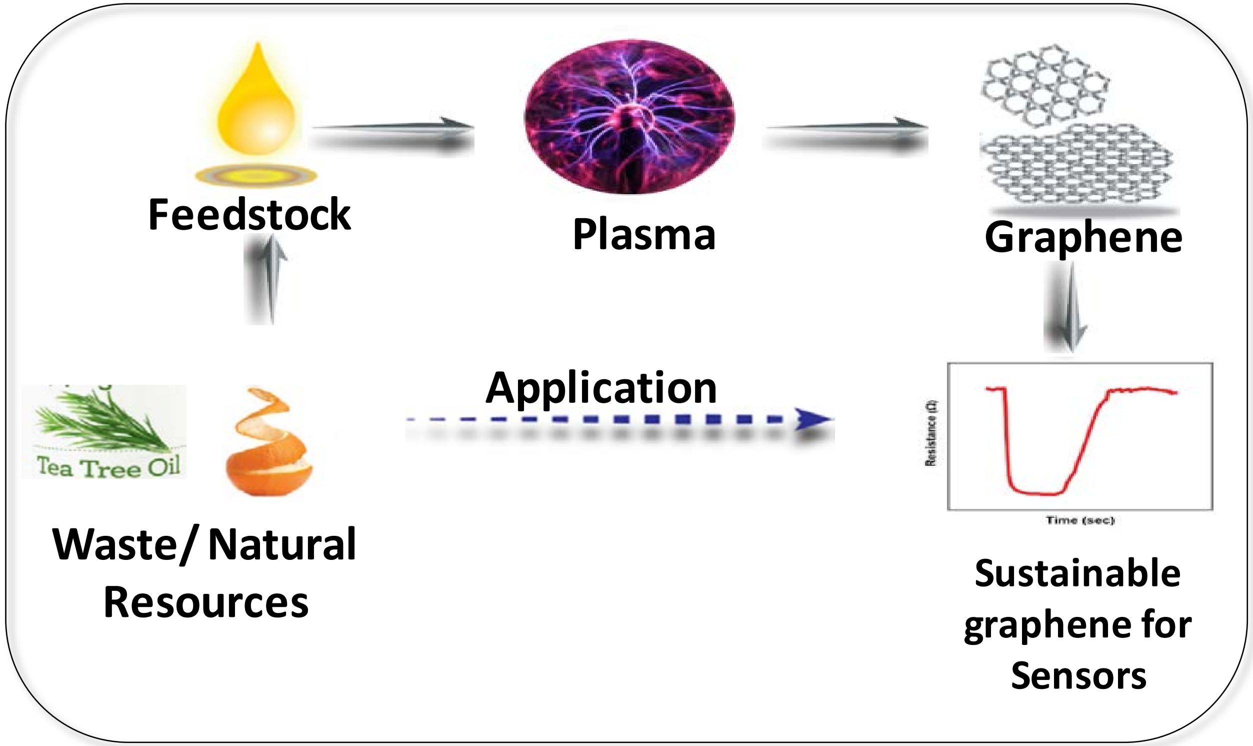
- Microwave Generator (Magnetron or Solid State)

Radio Frequency (~0.1 - 100 MHz)

- Capacitively Coupled RF Plasma
- Inductively Coupled RF Plasma (ICP)
- Helicon (Magnetically enhanced wave coupling)

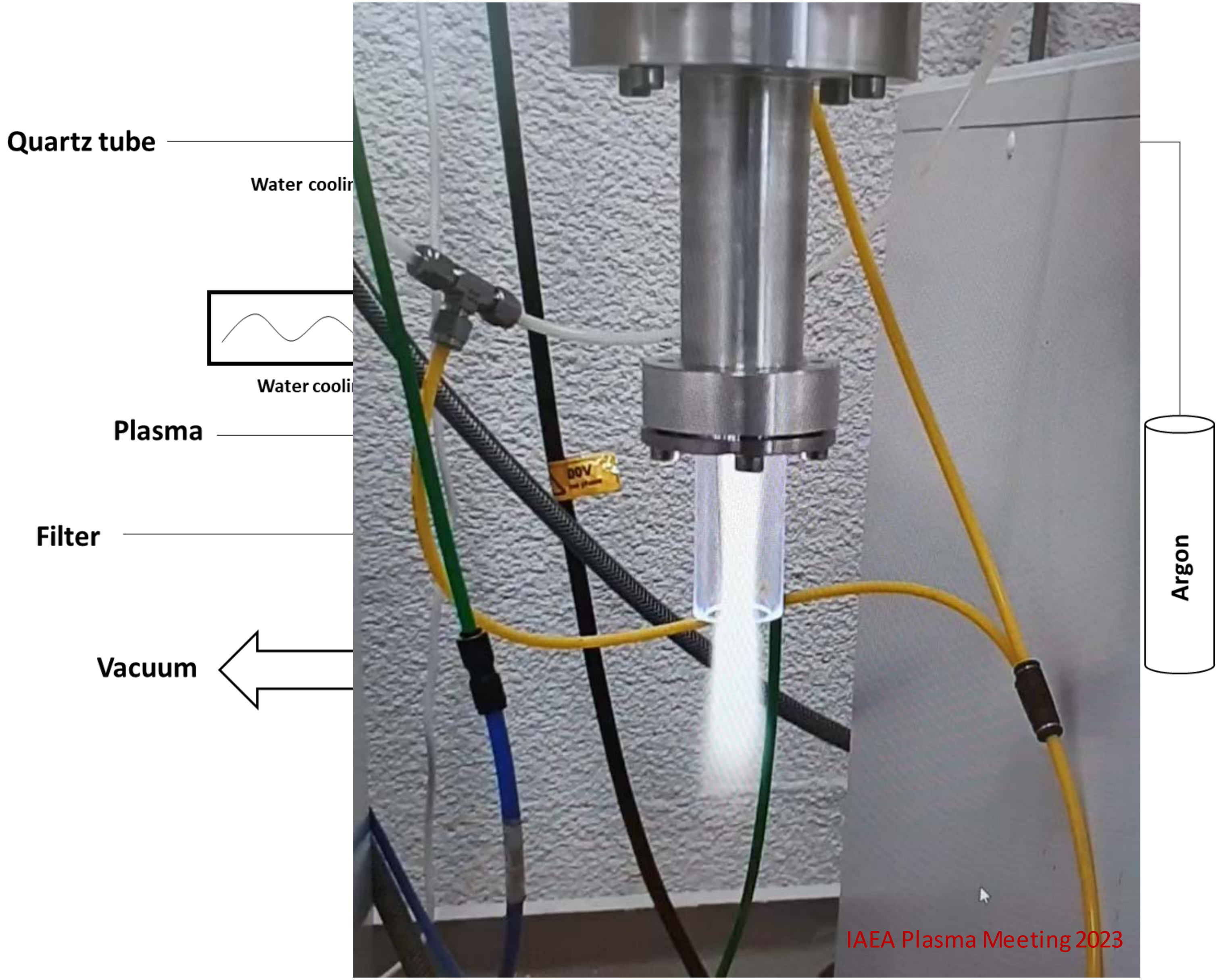
Synthesis of nanomaterials from sustainable sources





Microwave Plasma: Synthesis of graphene

Bottom-up method for graphene synthesis



- ✓ Substrate-free
- ✓ Process at atmospheric pressure
- ✓ No pre-heating
- ✓ No need of hydrogen gas
- ✓ Scalable
- ✓ High production rate
- ✓ Short processing time (few seconds)

- Energy intensive
- Requires precise control of parameters

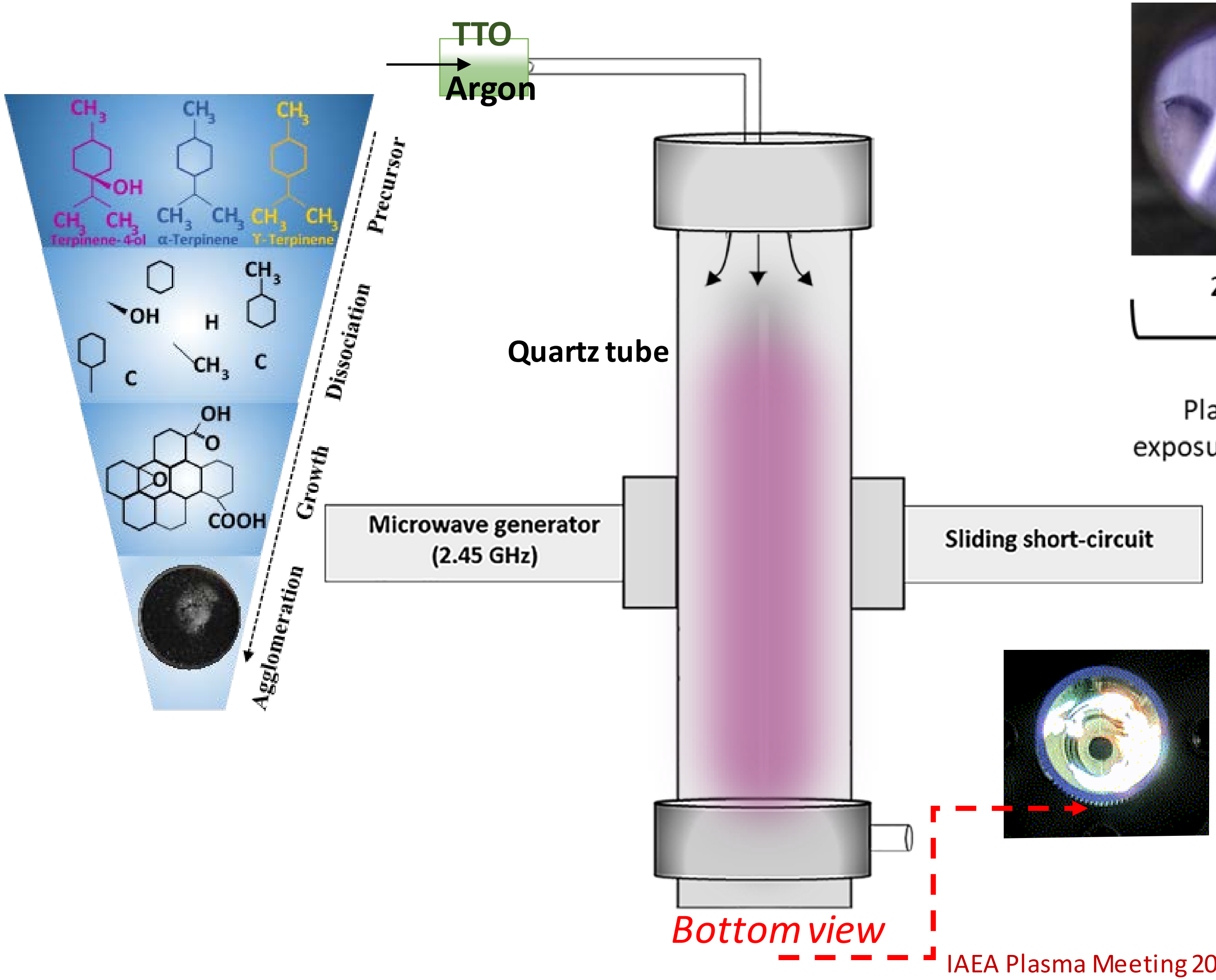
Microwave Plasma: Synthesis of graphene

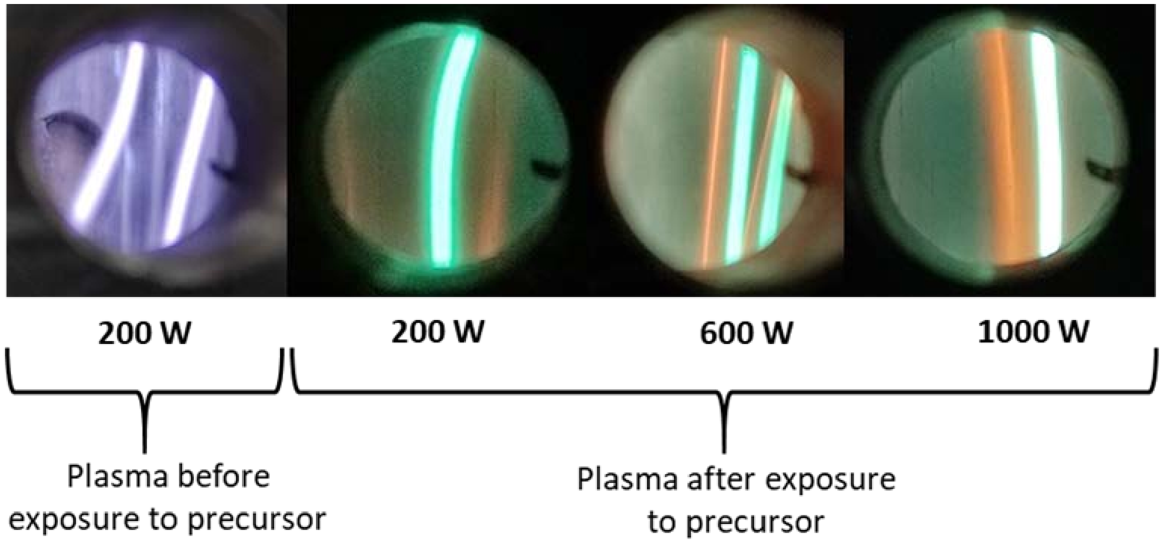
- Tea Tree Oil → Graphene
- Tea Tree Oil + Silver nitrate → Silver-graphene nanocomposite
- Tangerine (orange peel) oil → Graphene
- Aniline → Nitrogen-doped graphene oxide

JCU

Microwave Plasma: Synthesis of graphene

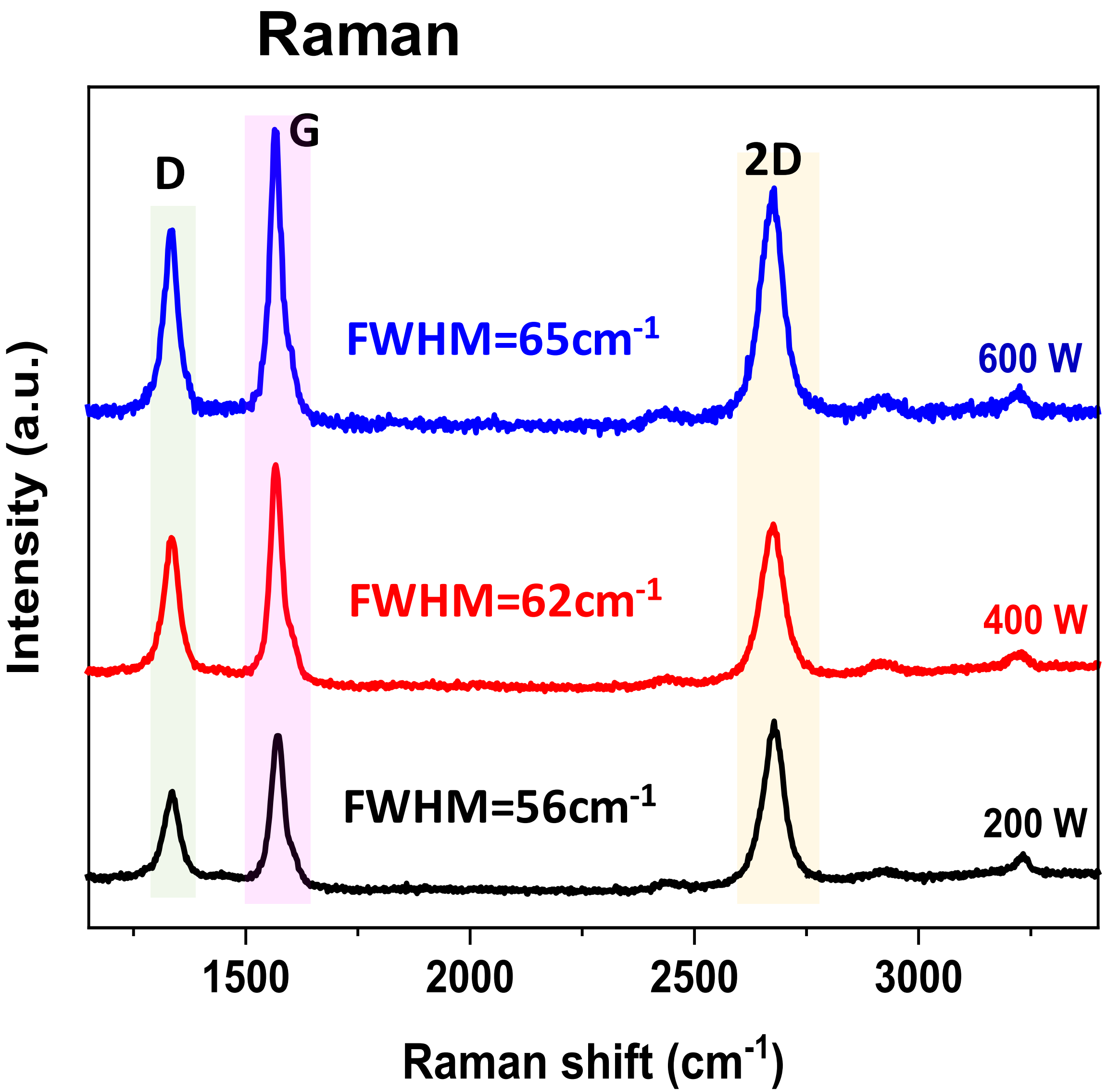
From Tea Tree Oil (TTO)

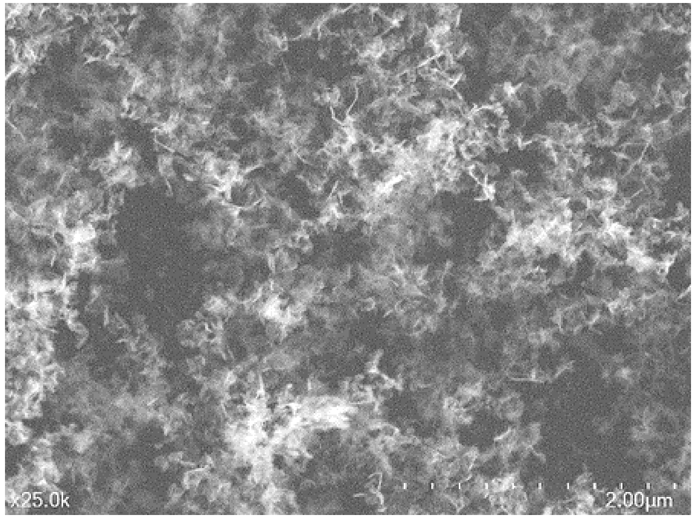


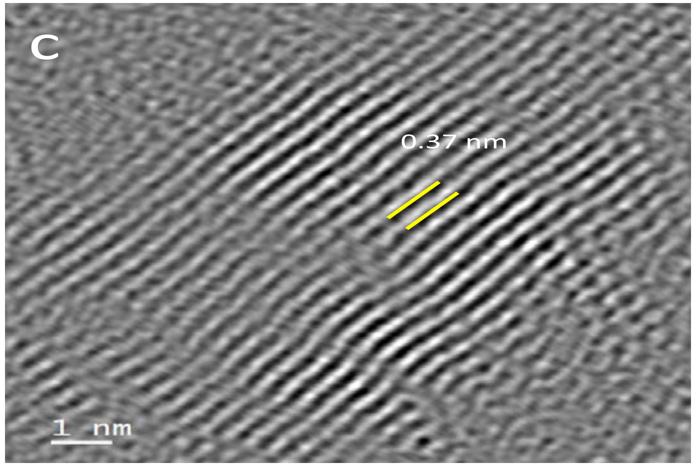


Zafar, M. Adeel, et al. "Plasma-Based Synthesis of Freestanding Graphene from a Natural Resource for Sensing Application." Advanced Materials Interfaces 10.11 (2023): 2202399.

Microwave Plasma Graphene: TTO







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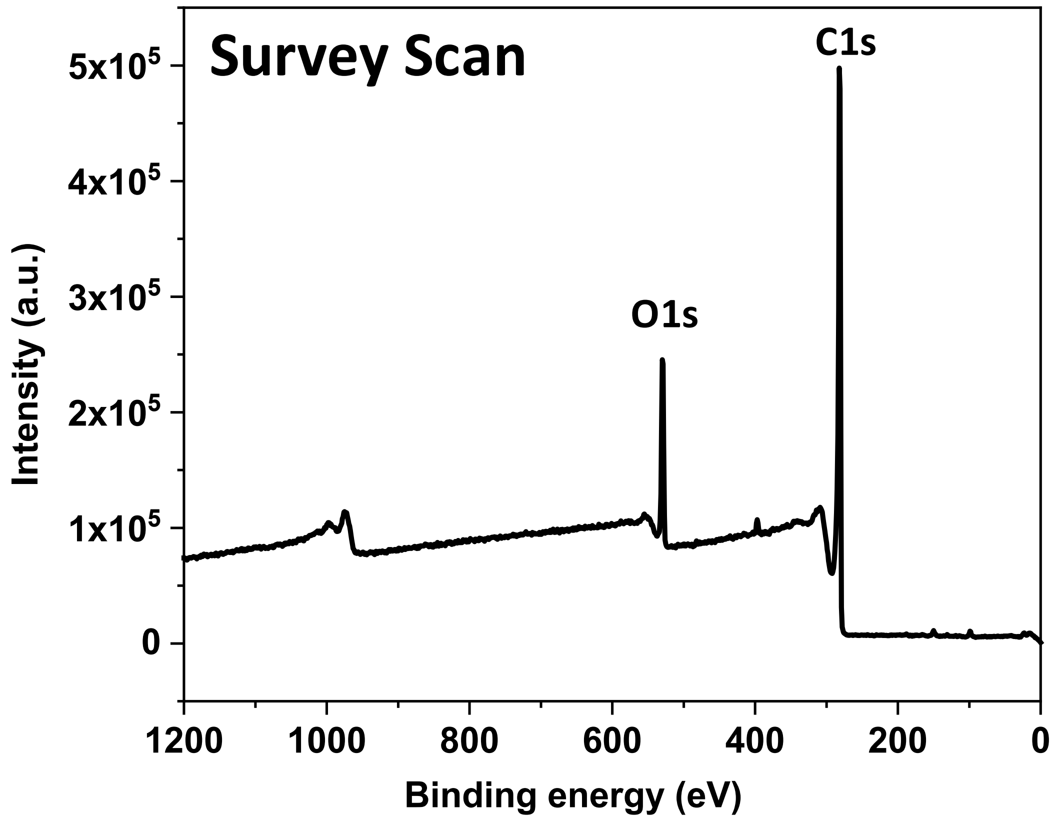
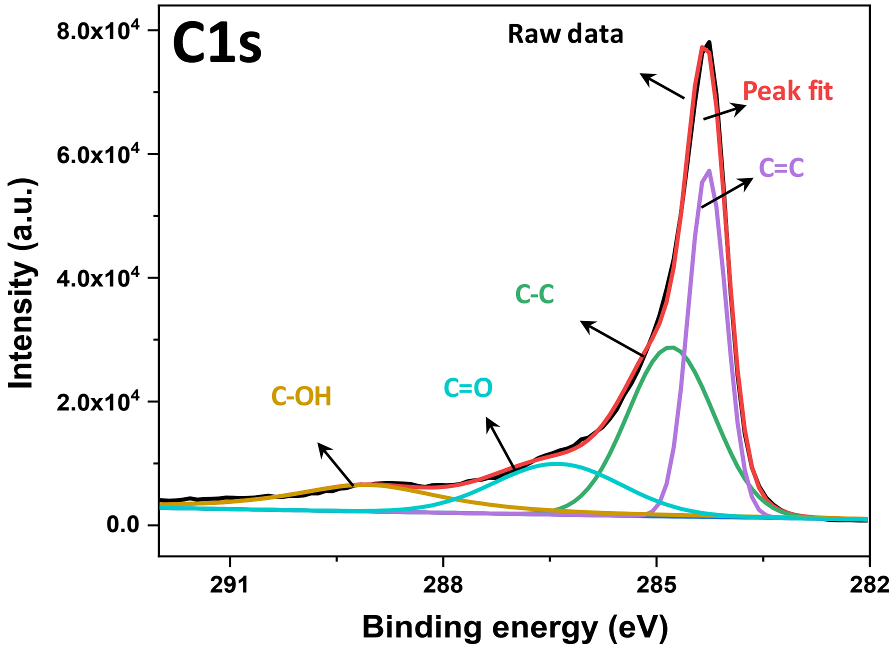
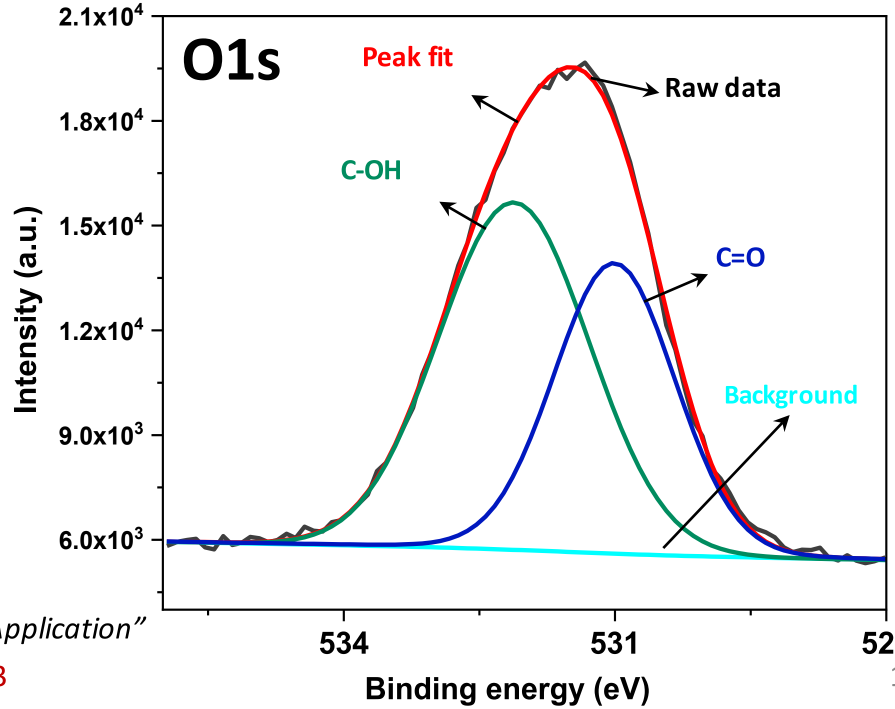
Microwave Plasma Graphene: TTO

XPS spectrum







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Microwave Plasma Graphene: Rate of production

Precursor	Microwave power (W)	Precursor flow rate (sccm)	I_D/I_G	Number of layers	Production rate (mg/min)	Ref.
Ethanol	250	0.3	-	Mono-and bi-layers	2	[10, 25]
Ethanol	900	0.5 – 3.5	-	Few layers	2	[48]
Ethanol	200	0.0036	0.6	Multilayers	0.07	[49]
Ethanol	300	0.33	0.24	Few layers	1.33	[24]
Ethanol	300	0.048	0.35	Few to multilayers	1.45	[50]
Methane	1000	2 – 8	0.62	Multilayers	-	[30]
Methane	1200-1400	-	1.57 or 1.77	Few to multilayers	-	[51]
Tea tree oil	**200**	**0.3**	**0.83**	**Multilayers**	**1.57**	**This work**

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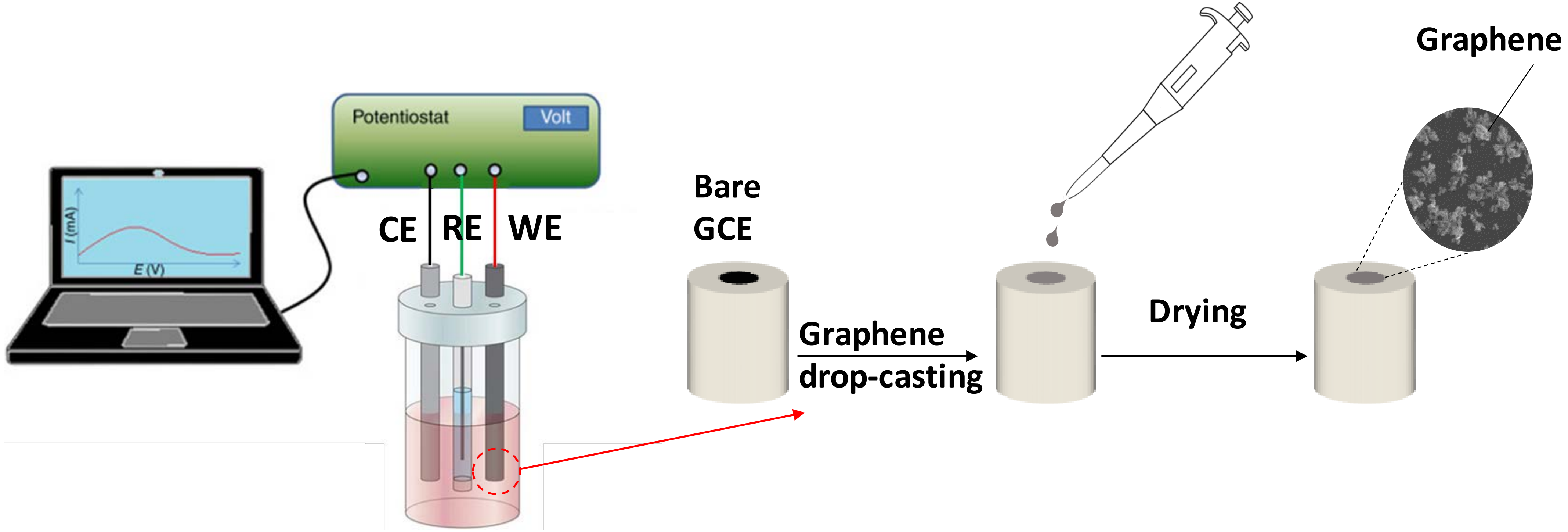
Microwave Plasma: graphene sensor for diuron detection

- Prolong use of diuron herbicide contaminate crops and water
- Toxic for humans and aquatic organisms
- Genotoxic and Interfere hormones



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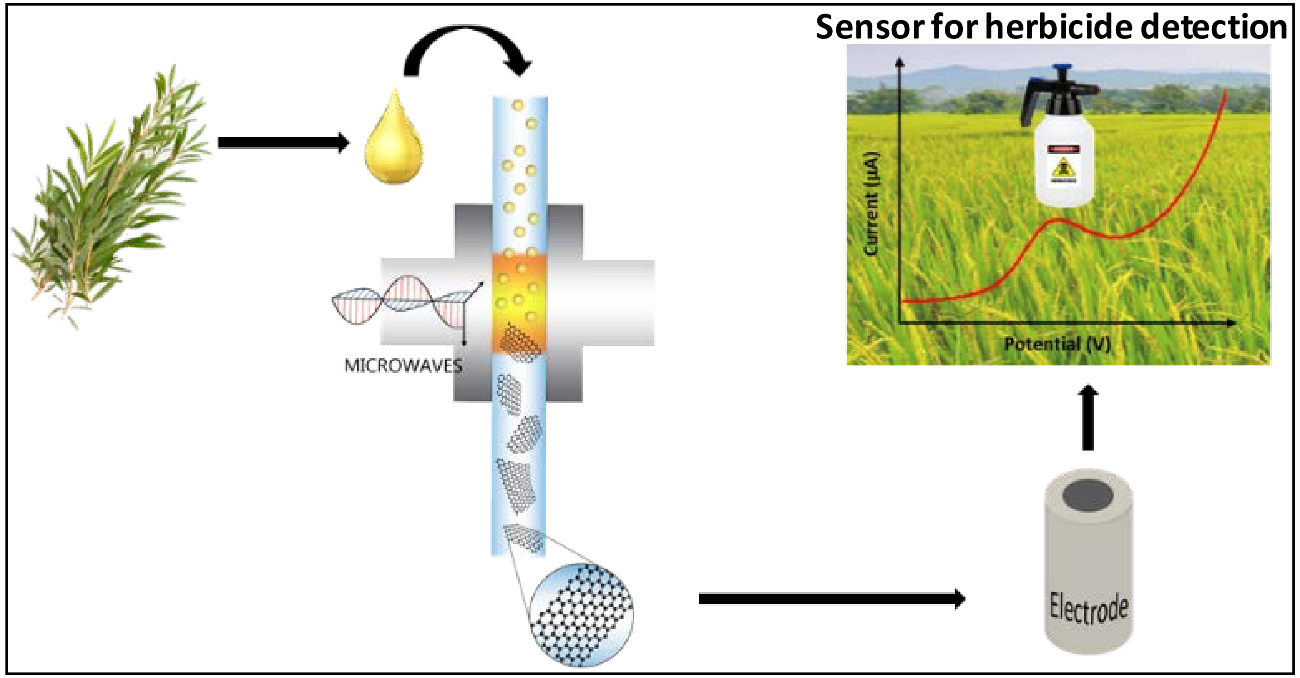
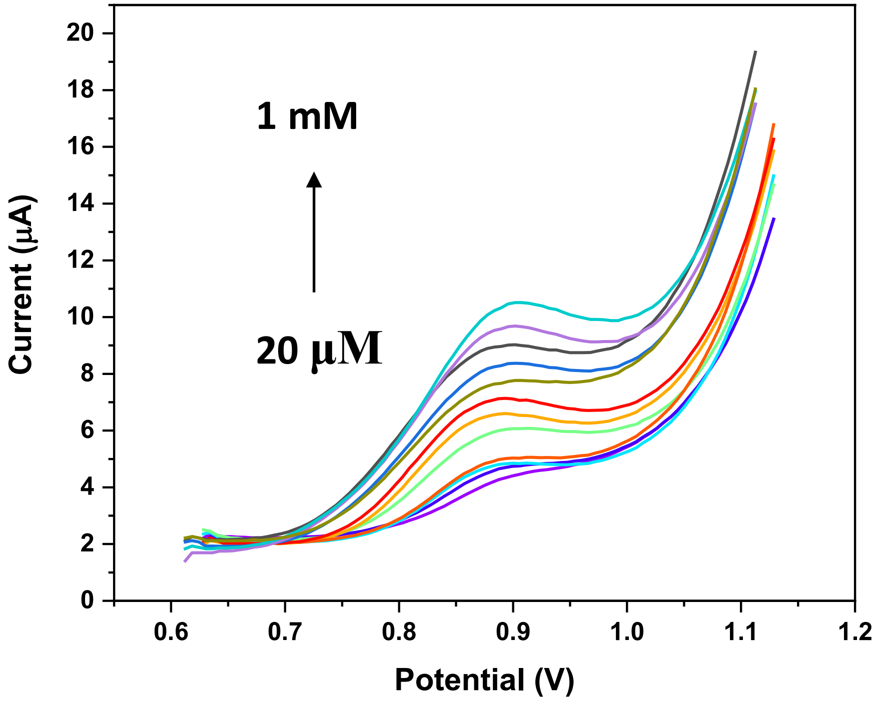
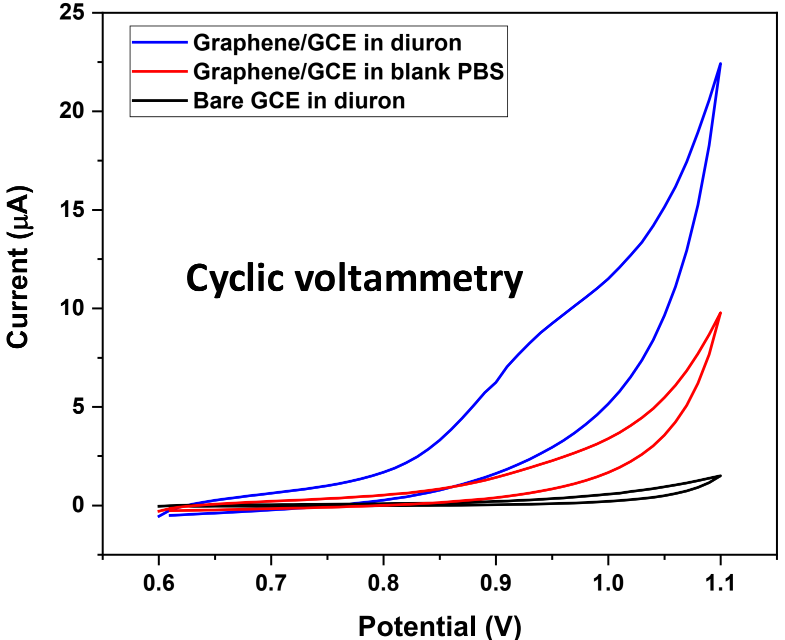
Microwave Plasma: graphene sensor for diuron detection



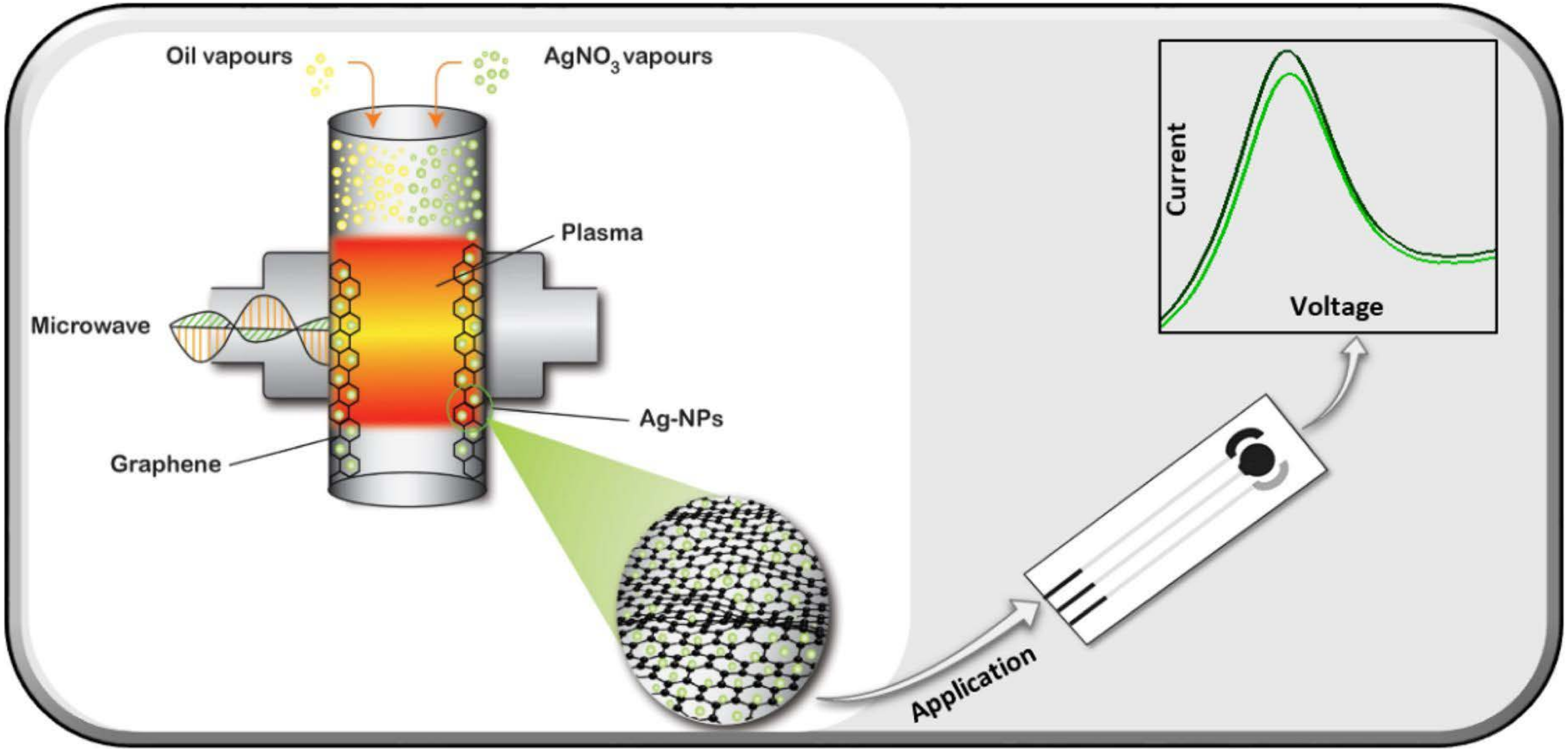


Differential pulse voltammetry (DPV) curves at graphene/GCE for different concentrations (20, 80, 120, 180, 300, 400, 500, 600, 700, 800, 900, 1000 µM) of **diuron** in 0.1 M PBS



★ **Limit of detection (LOD) = 5 µM**

Rapid and chemical-free synthesis of graphene-Ag nanocomposite using plasma

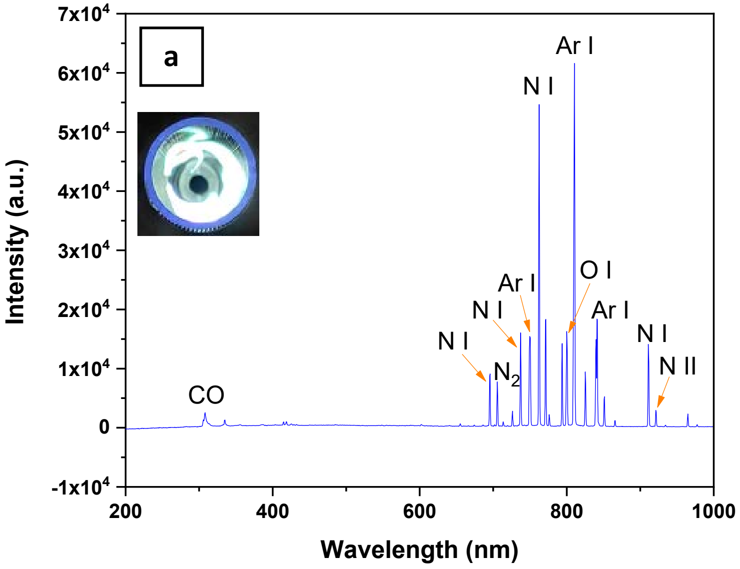


Zafar, M. Adeel, et al. "Expeditious and Eco-friendly fabrication of Graphene-Ag nanocomposite for methyl paraben sensing." Applied Surface Science 638 (2023): 158006.

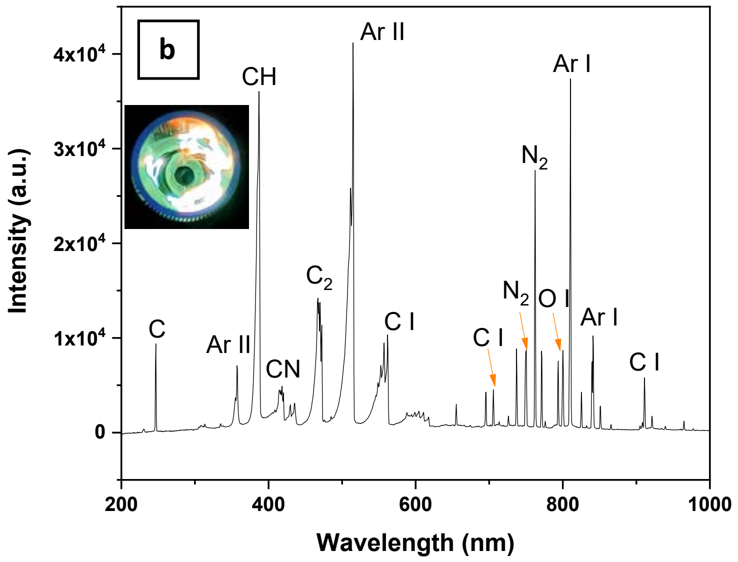
Microwave Plasma: Synthesis of graphene-Ag nanocomposite

Optical emission spectroscopy

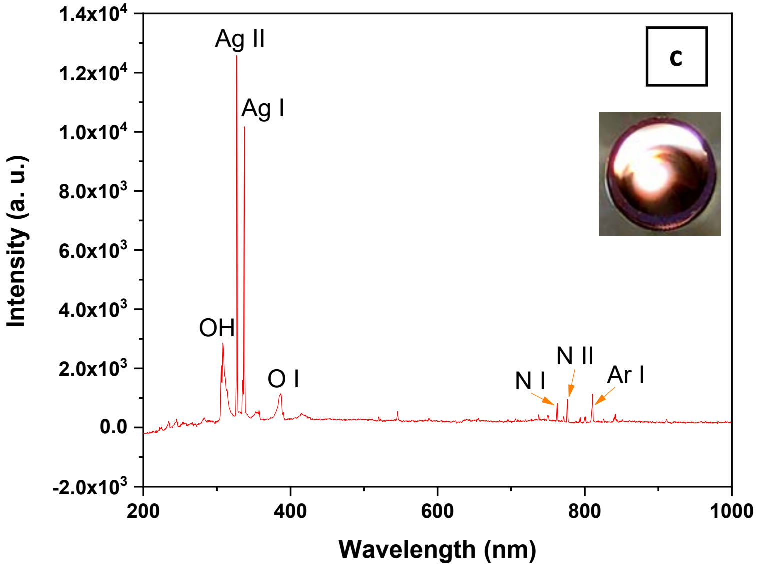
Pure Ar



Ar + tea tree vapors



Ar + 0.1 M $AgNO_3$



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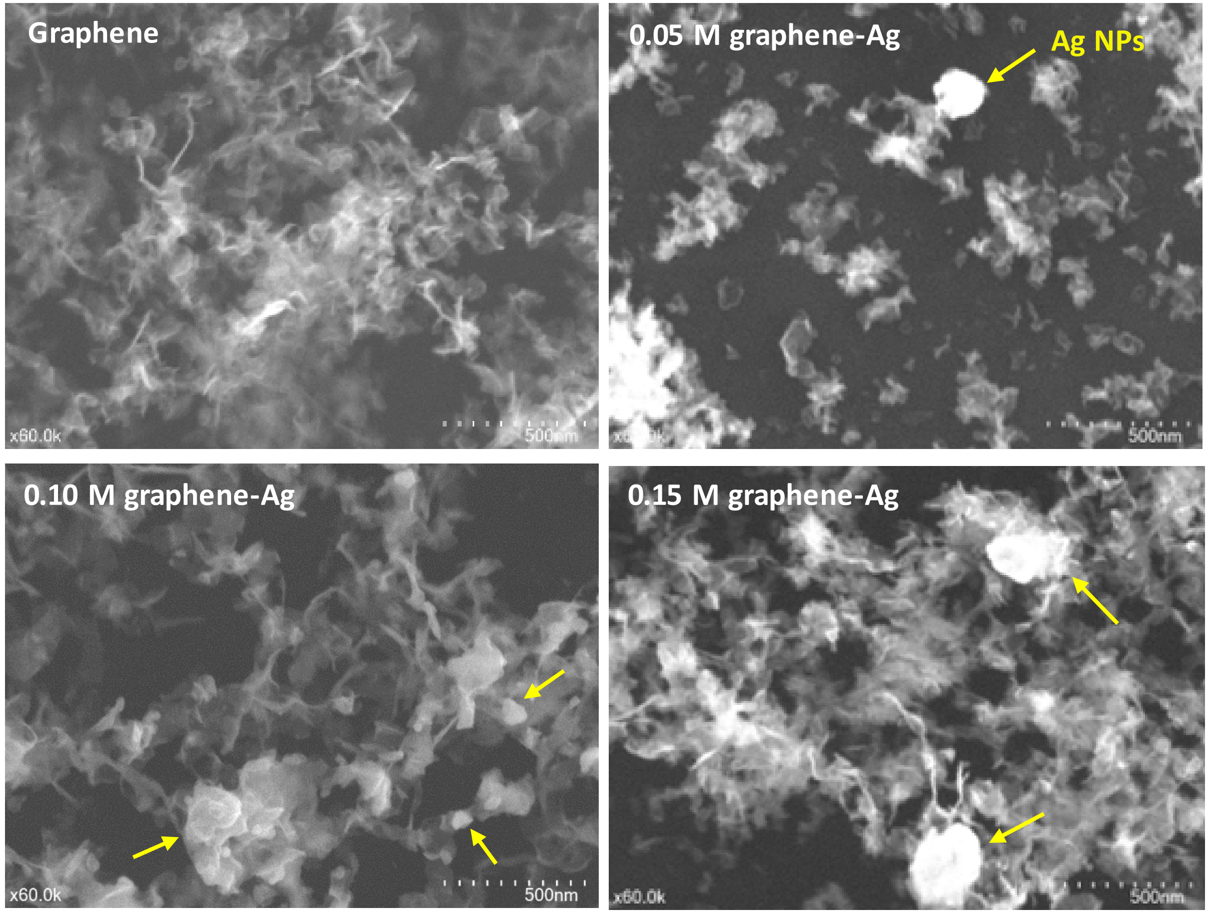
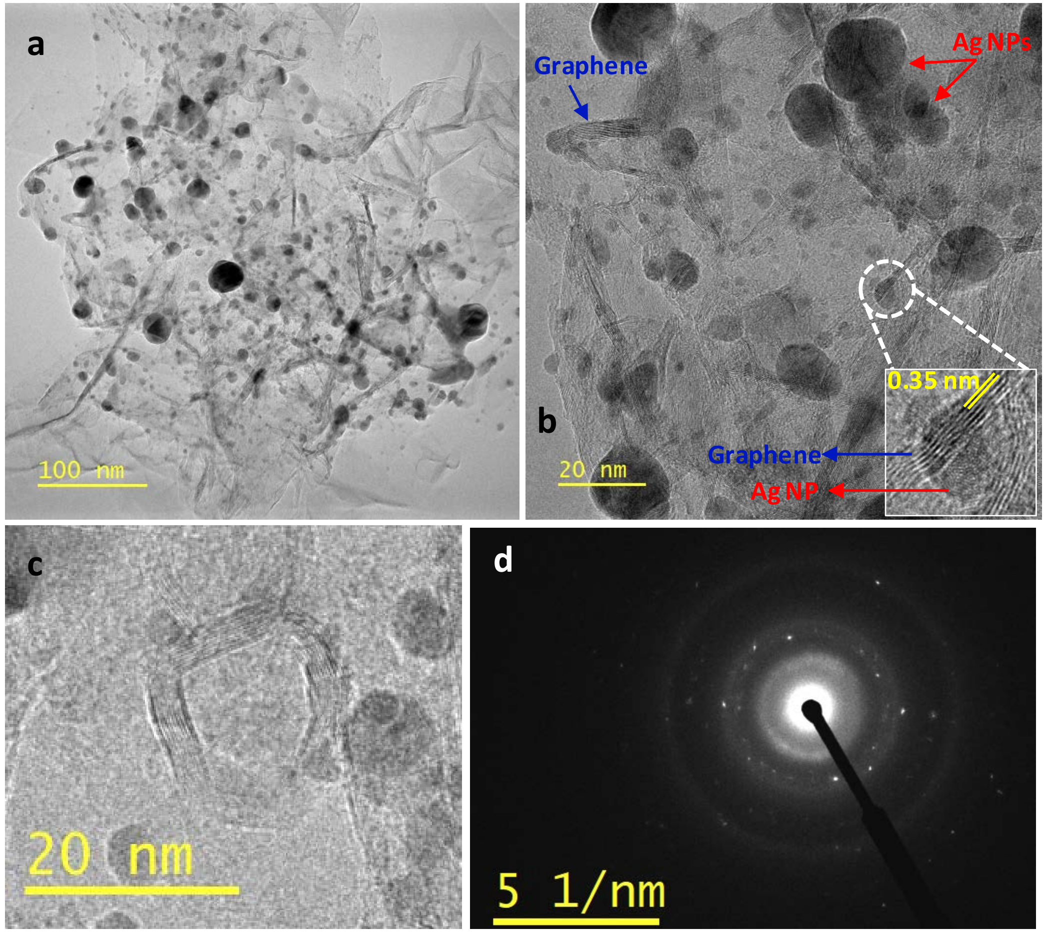
Microwave Plasma: Synthesis of graphene-Ag nanocomposite

SEM images



TEM images *(0.1 M $AgNO_3$ sample)*



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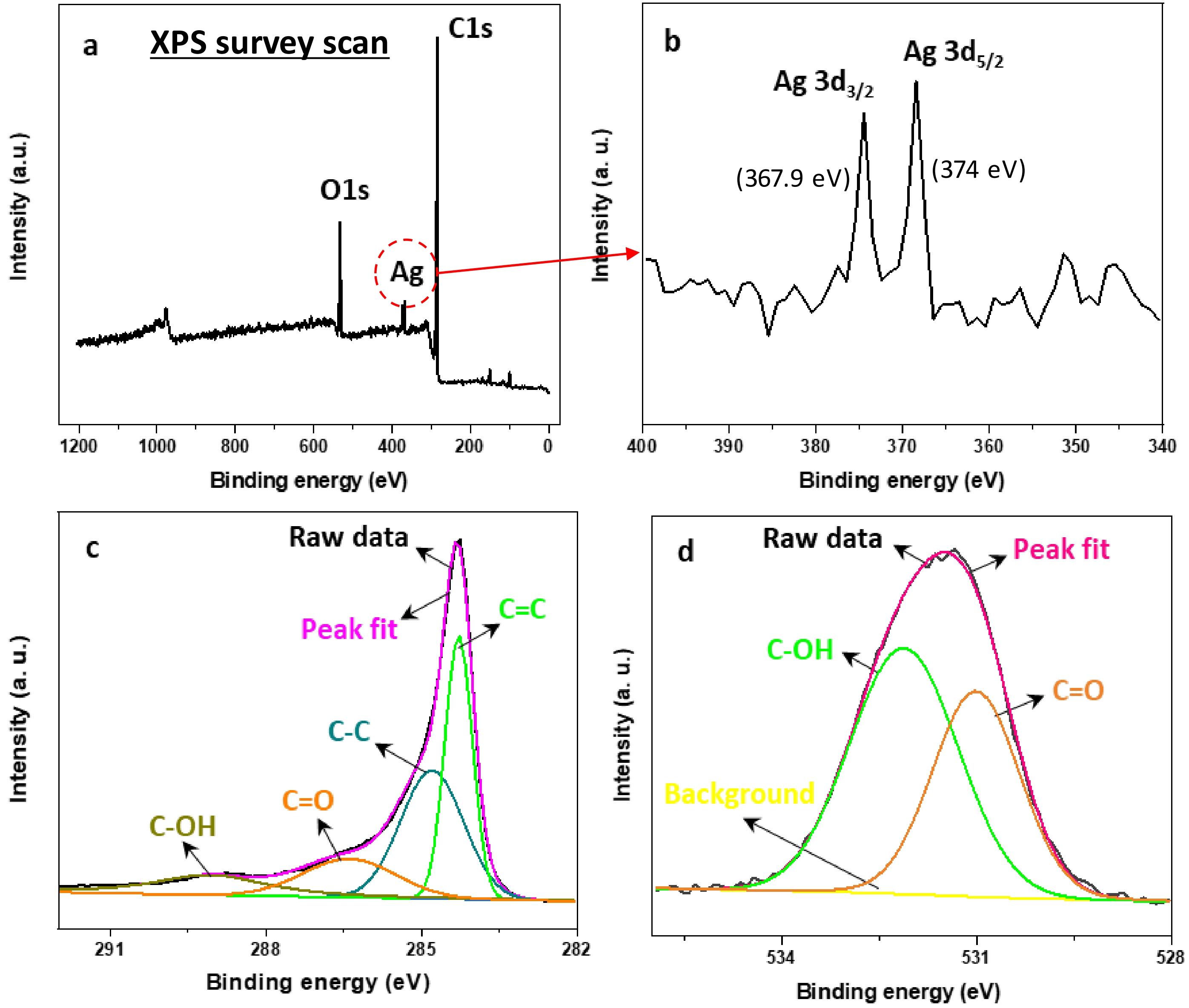
Microwave Plasma: Synthesis of graphene-Ag nanocomposite

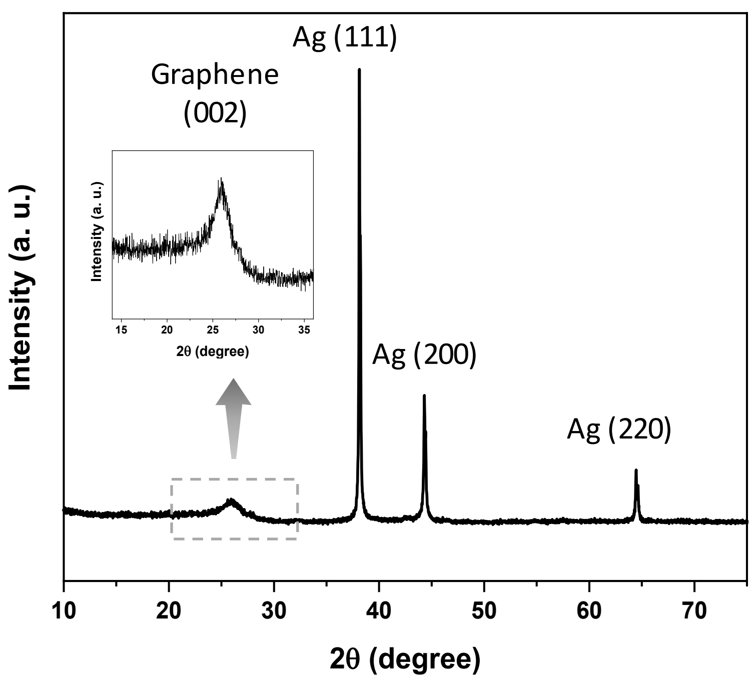


High resolution C1s **High resolution O1s**

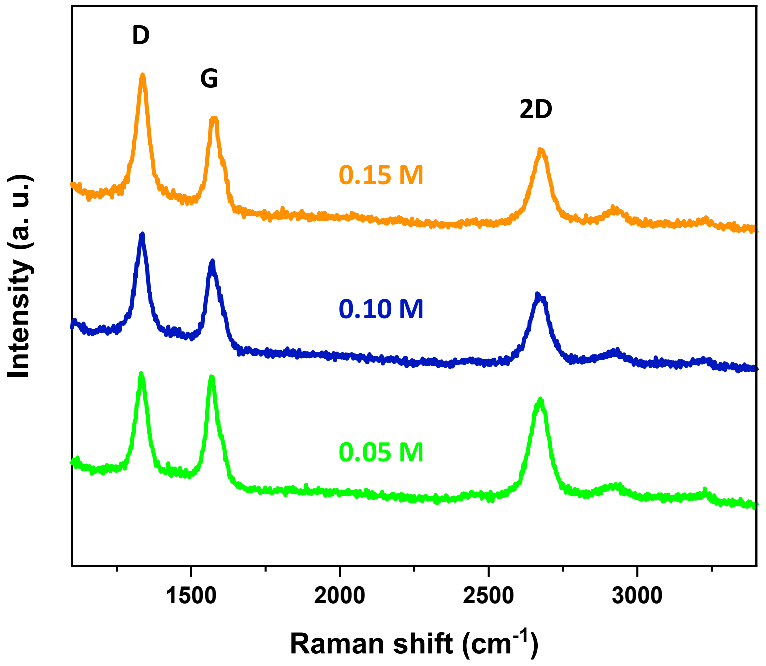
Ag metal
368.2 and 374.2 eV

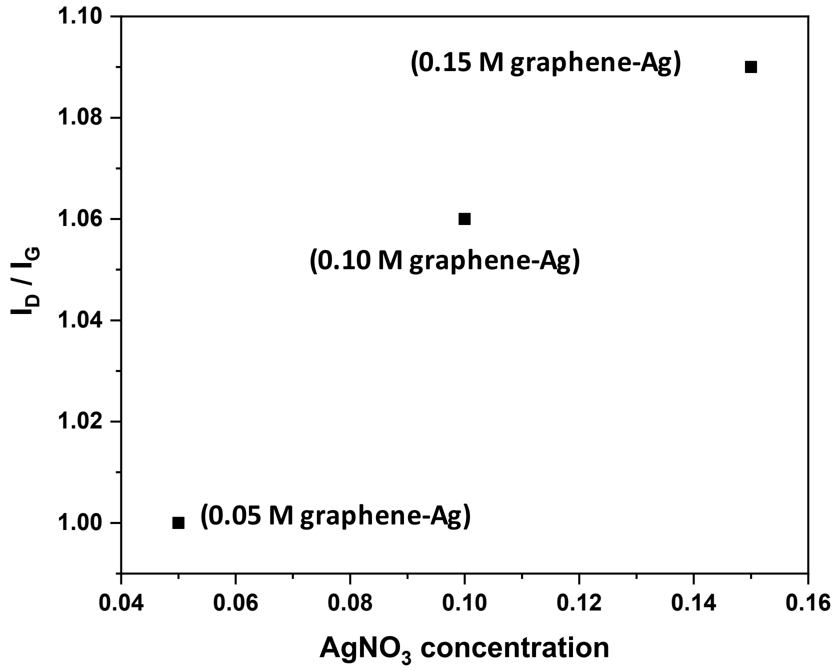
Microwave Plasma: Synthesis of graphene-Ag nanocomposite

XRD



Raman spectra





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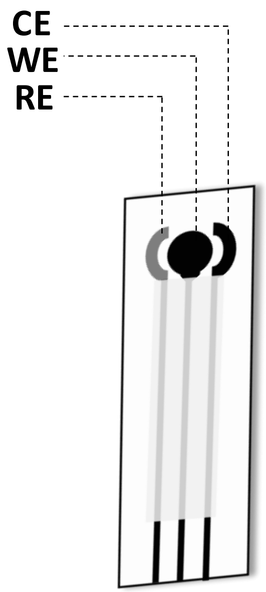
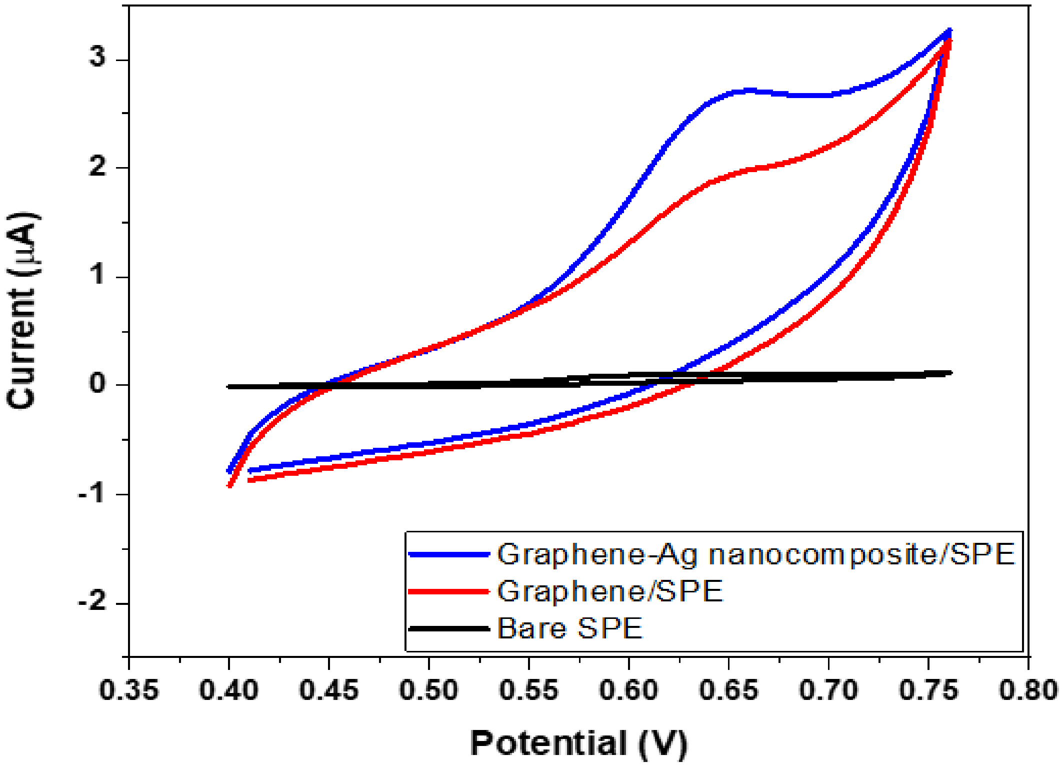
Microwave Plasma: graphene-Ag sensor for methyl paraben

- Paraben is typically used in cosmetics and is an endocrine-disrupting chemical
- Cause cancer
- Coral reef destruction
- Prohibited in sun blocks



Screen printed electrode (SPE)



Cyclic voltammograms in 0.1 M PBS (pH 7) containing 10 μM MP

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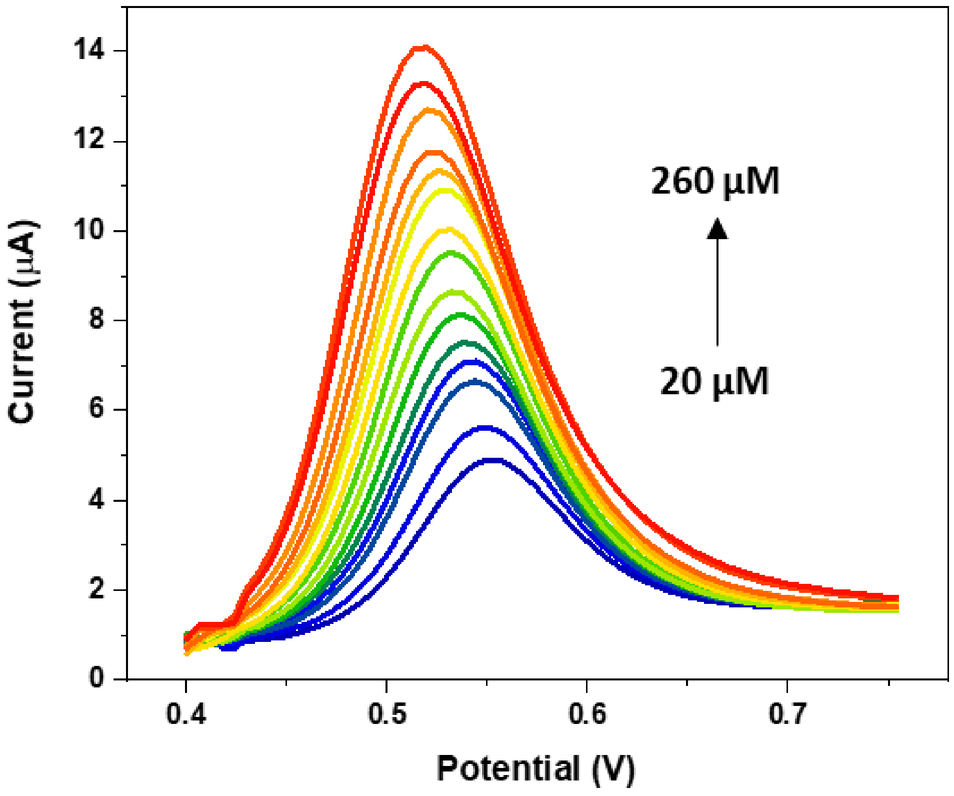
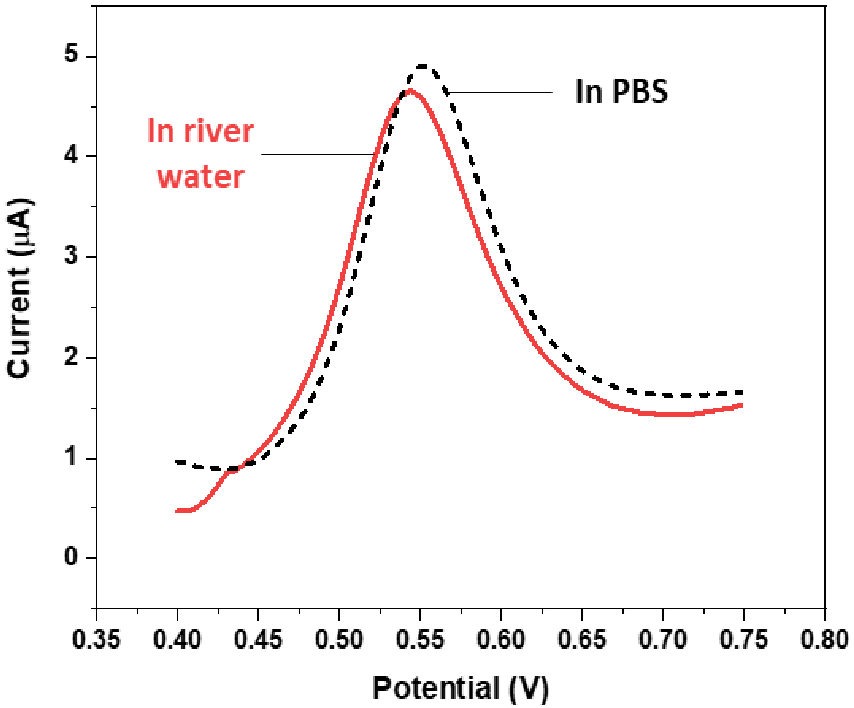
Microwave Plasma: graphene-Ag sensor for methyl paraben



DPV curves of different concentrations of MP (20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260 μM) in 0.1 M PBS (pH 7)

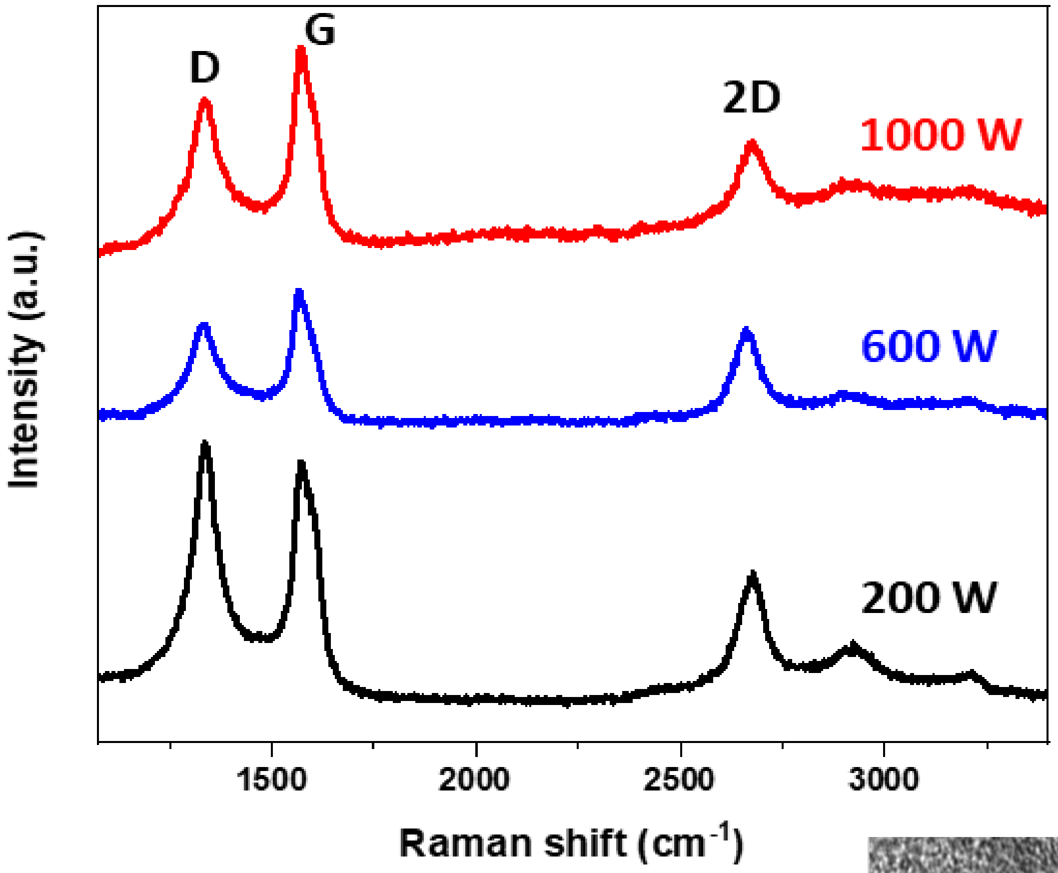
LOD = 2.5 μM

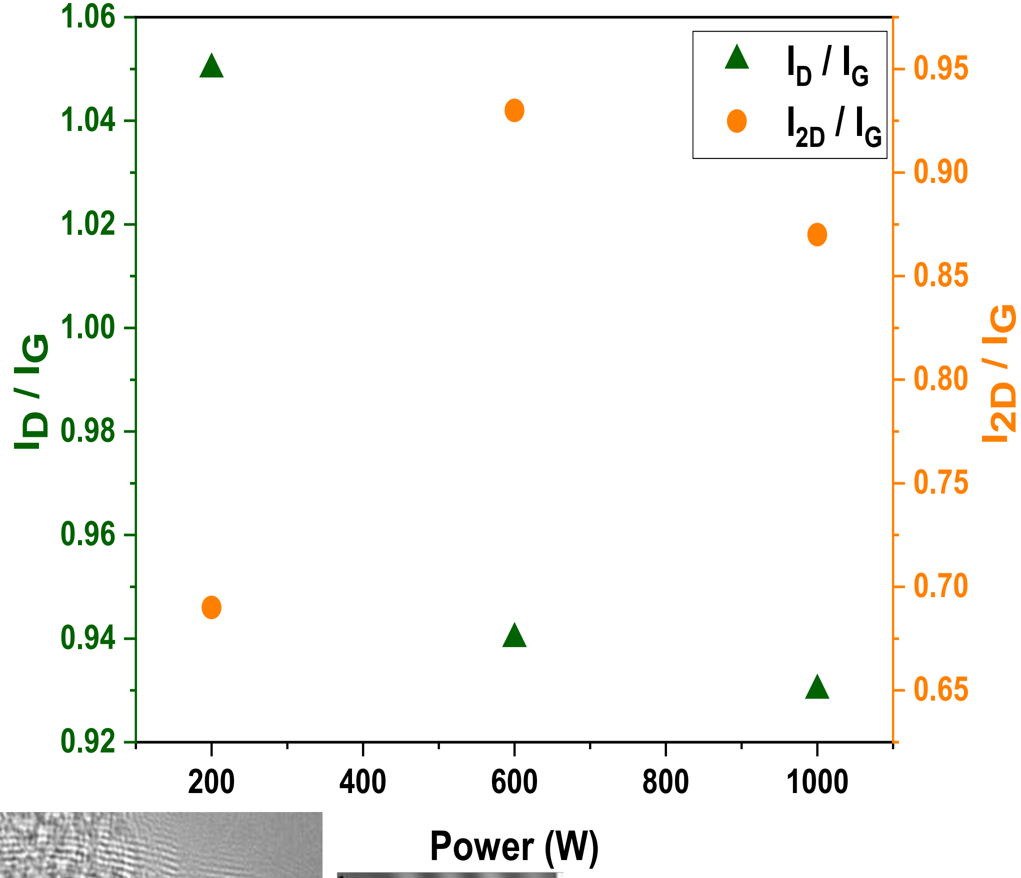


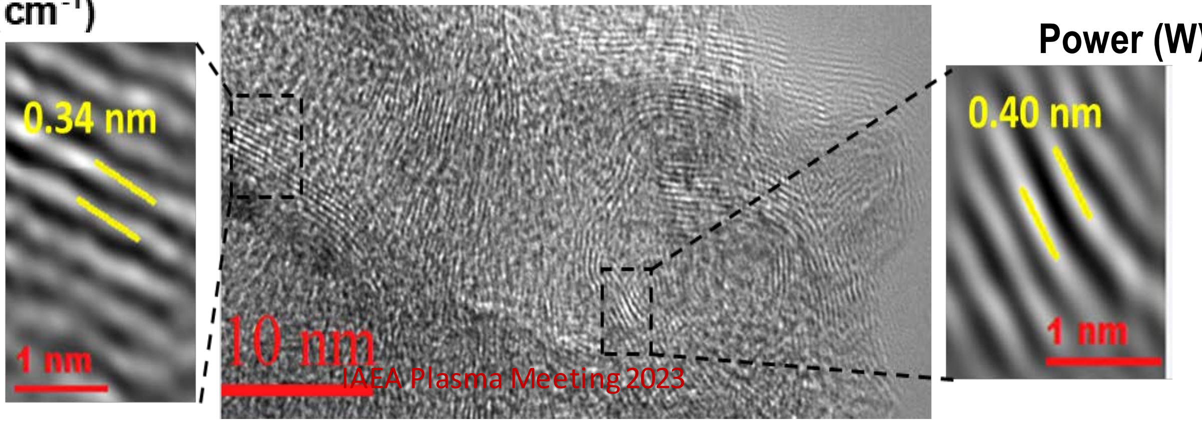
DPV curves of graphene-Ag nanocomposite/SPE in 0.1 M Phosphate Buffer Solution PBS (pH 7) and river water (pH 6.92) containing 20 μM

Zafar, M. Adeel, et al. "Expeditious and Eco-friendly fabrication of Graphene-Ag nanocomposite for methyl paraben sensing." Applied Surface Science 638 (2023): 158006.

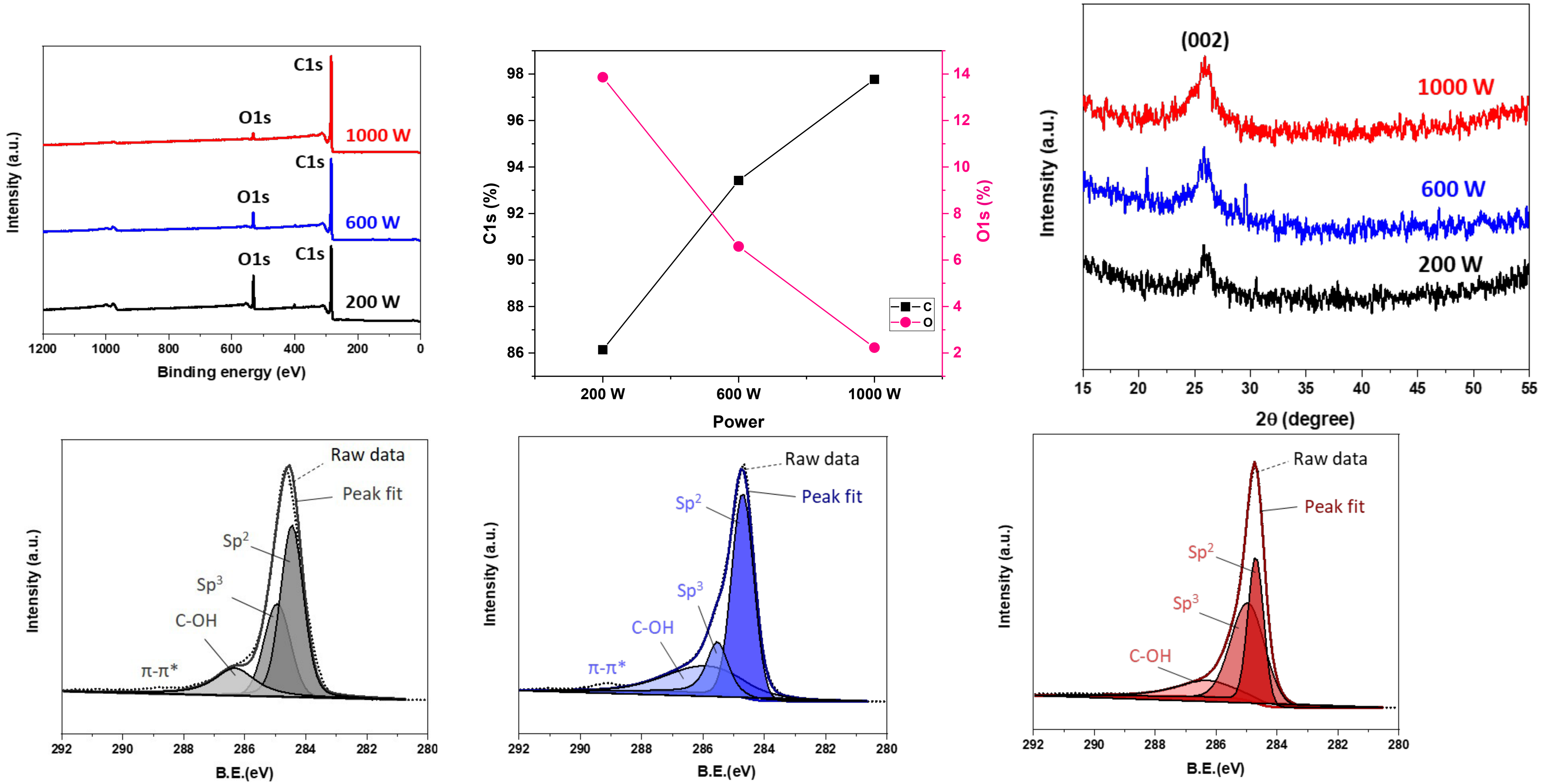
Synthesis of graphene from tangerine using Microwave Plasma







Microwave Plasma: Synthesis of graphene from tangerine



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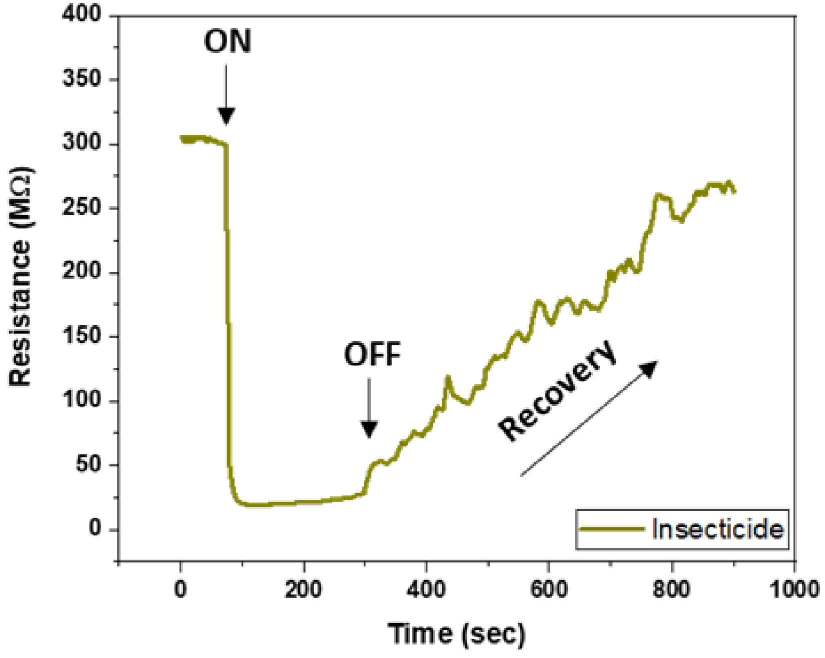
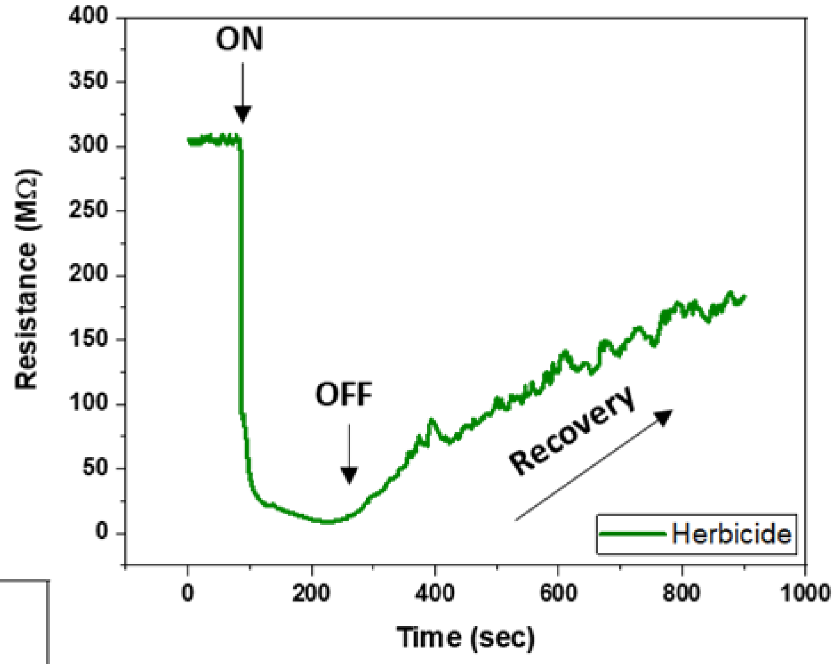
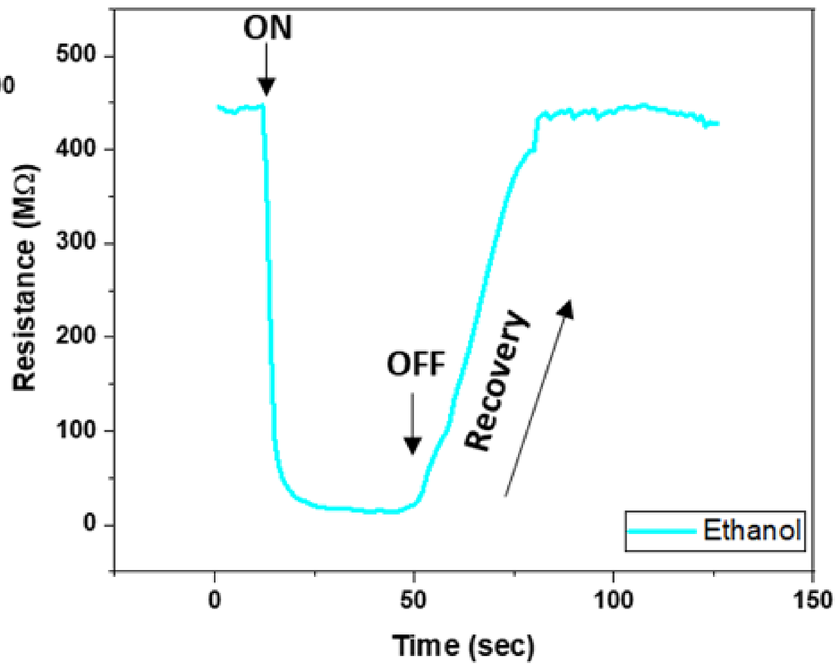
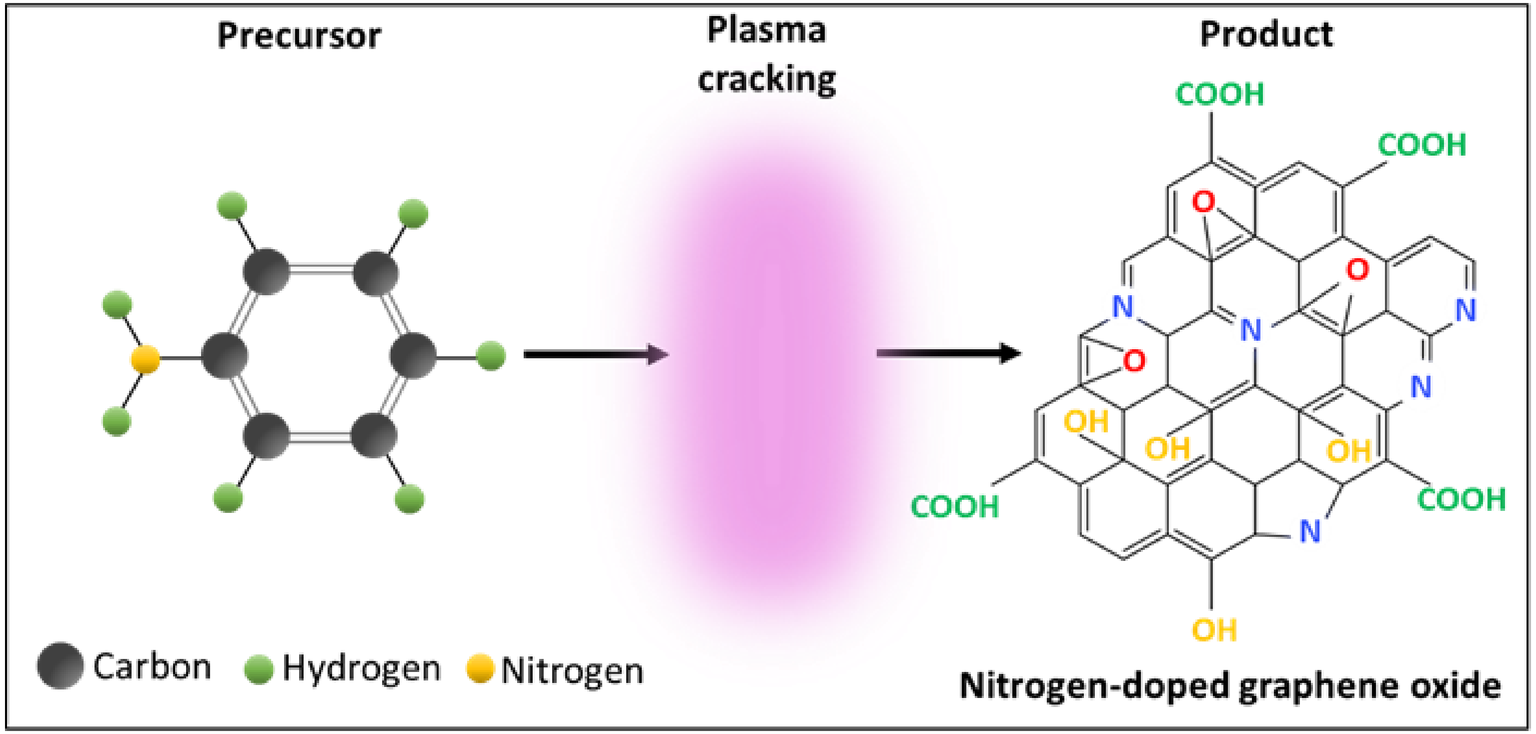
Microwave Plasma: Tangerine based graphene for vapour sensor





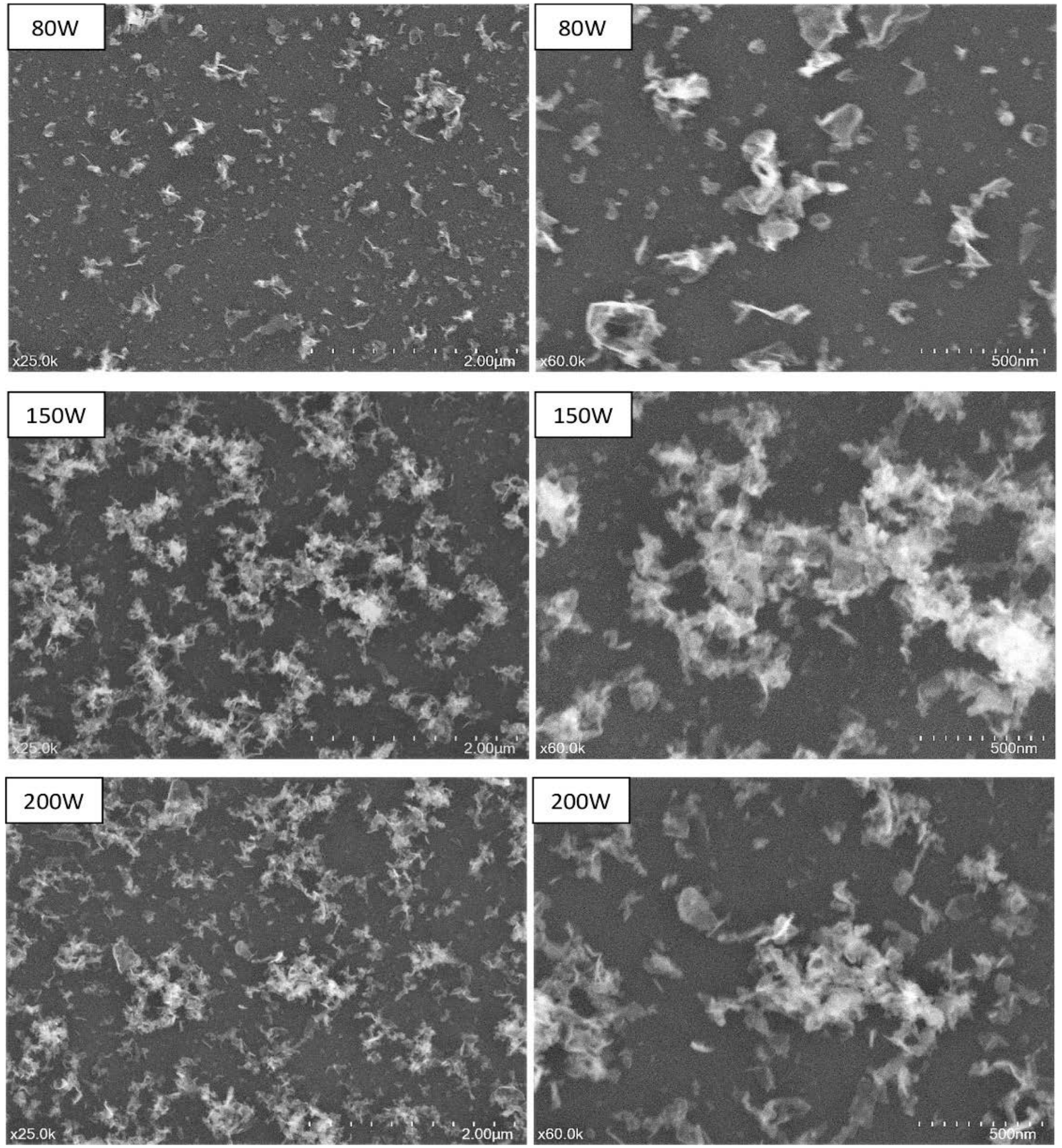


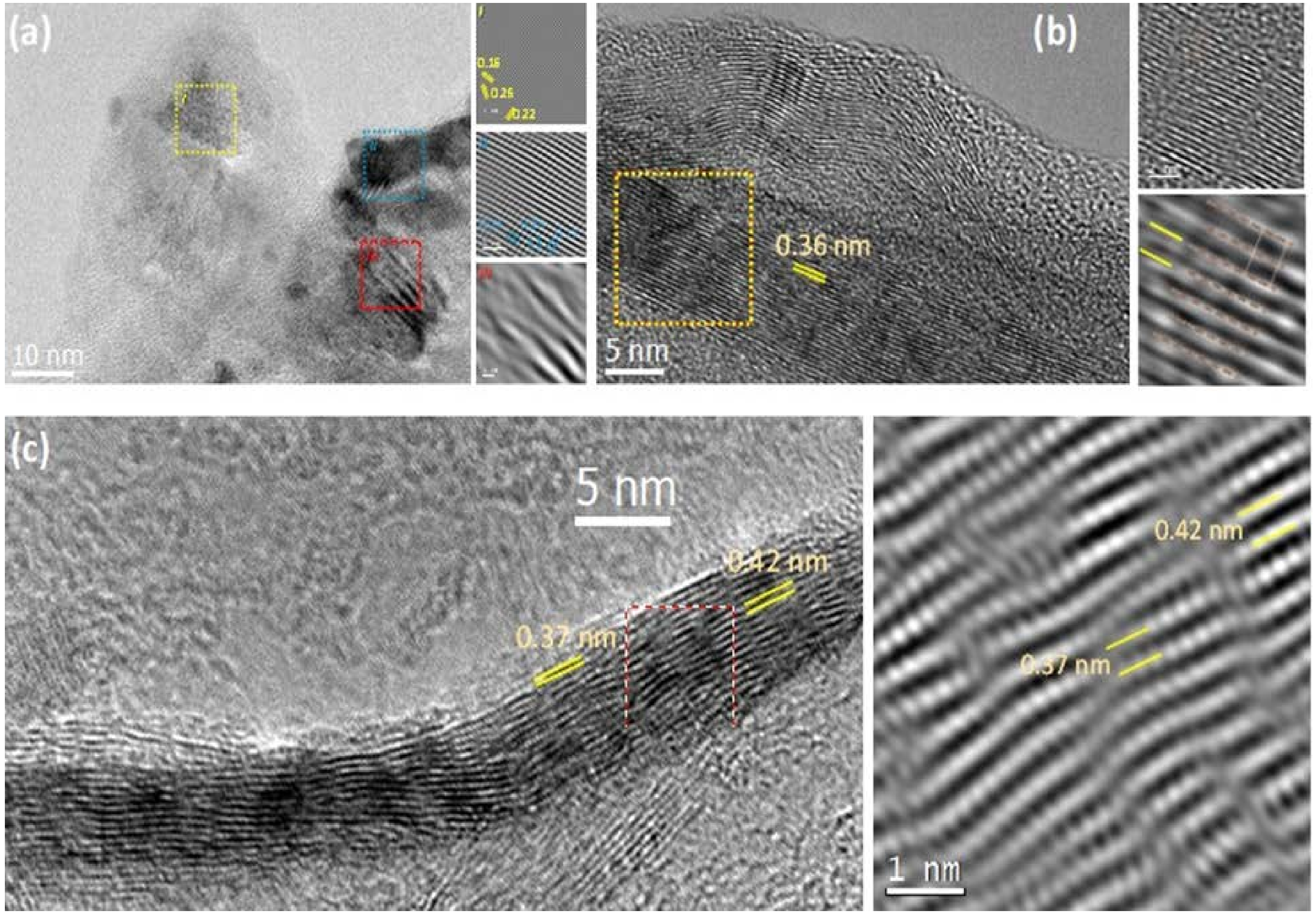
Synthesis of nitrogen-doped graphene oxide using Microwave Plasma in a single step



Zafar, M. A., Varghese, O. K., Robles Hernandez, F. C., Liu, Y., & Jacob, M. V. (2022). Single-Step Synthesis of Nitrogen-Doped Graphene Oxide from Aniline at Ambient Conditions. ACS Applied Materials & Interfaces.

Microwave Plasma: N-Graphene Oxide from Aniline





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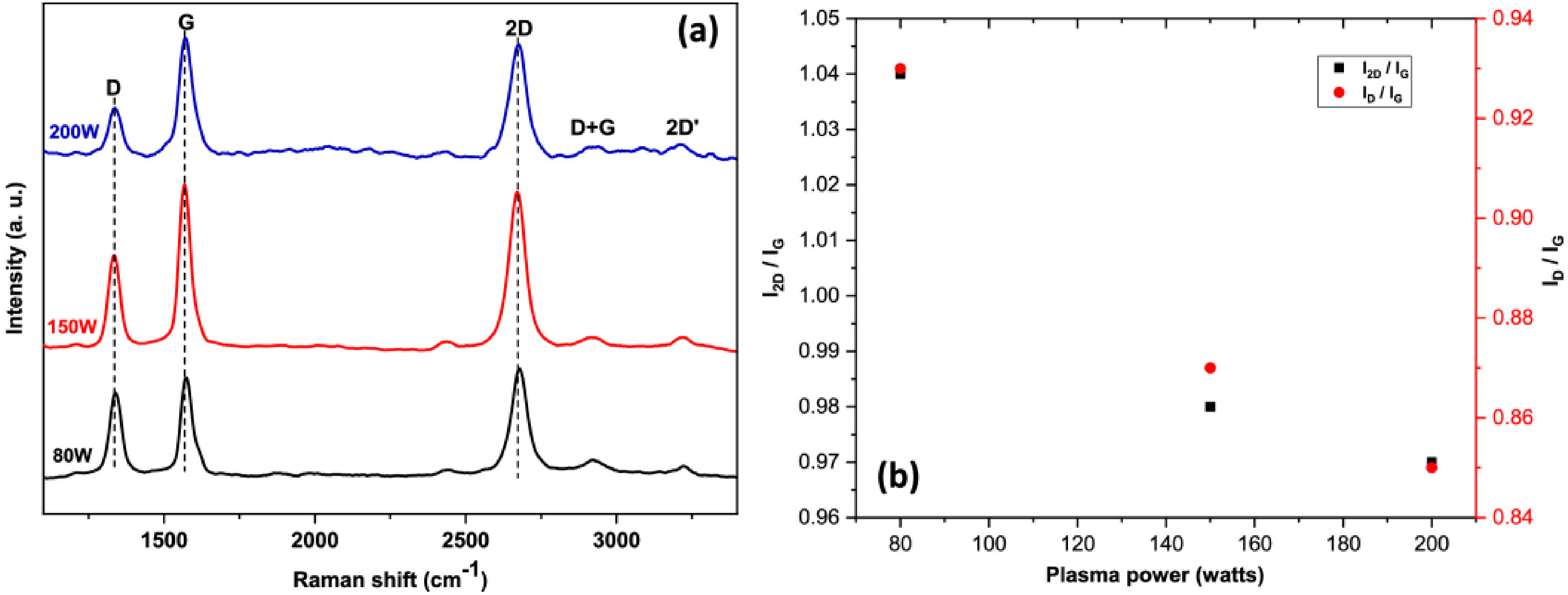

- Nitrogen-doped graphene oxide (N-GO) is formed in a single step. Oxygen comes from atmosphere due to ambient air synthesis
- Very low power (80 W) only needed to breakdown the precursor and form N-GO
- Production rate is ~2 mg/min

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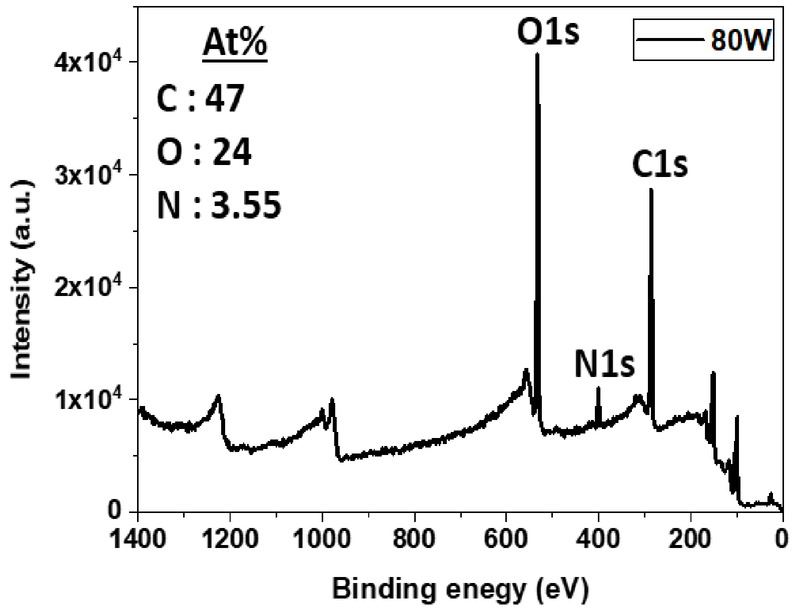

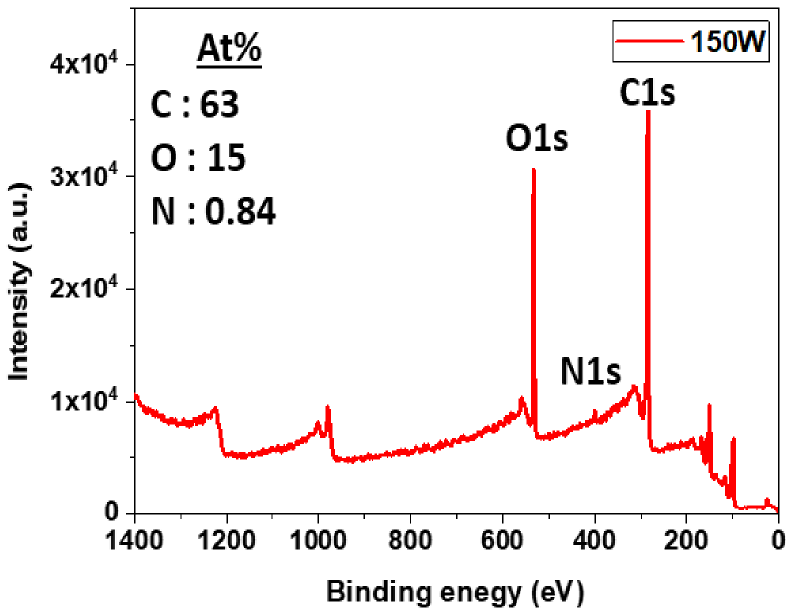

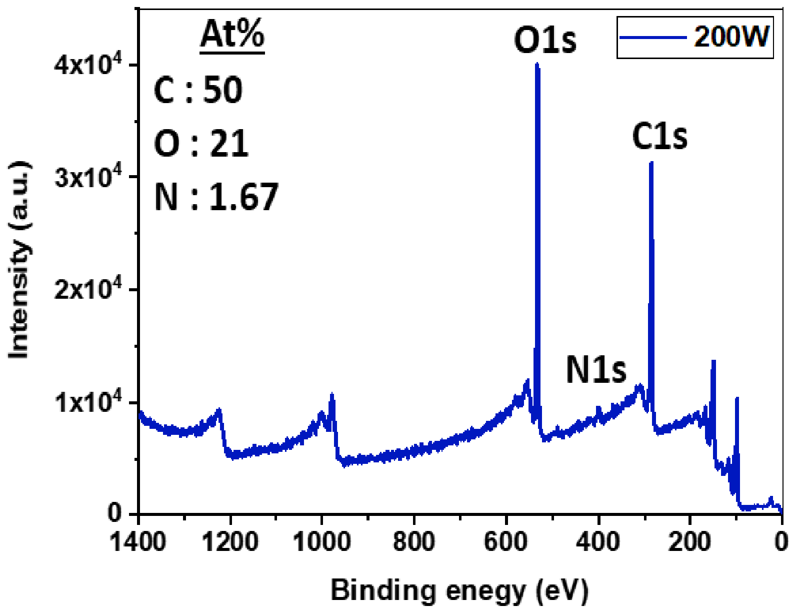

80 W, 150 W & 200 W microwave power

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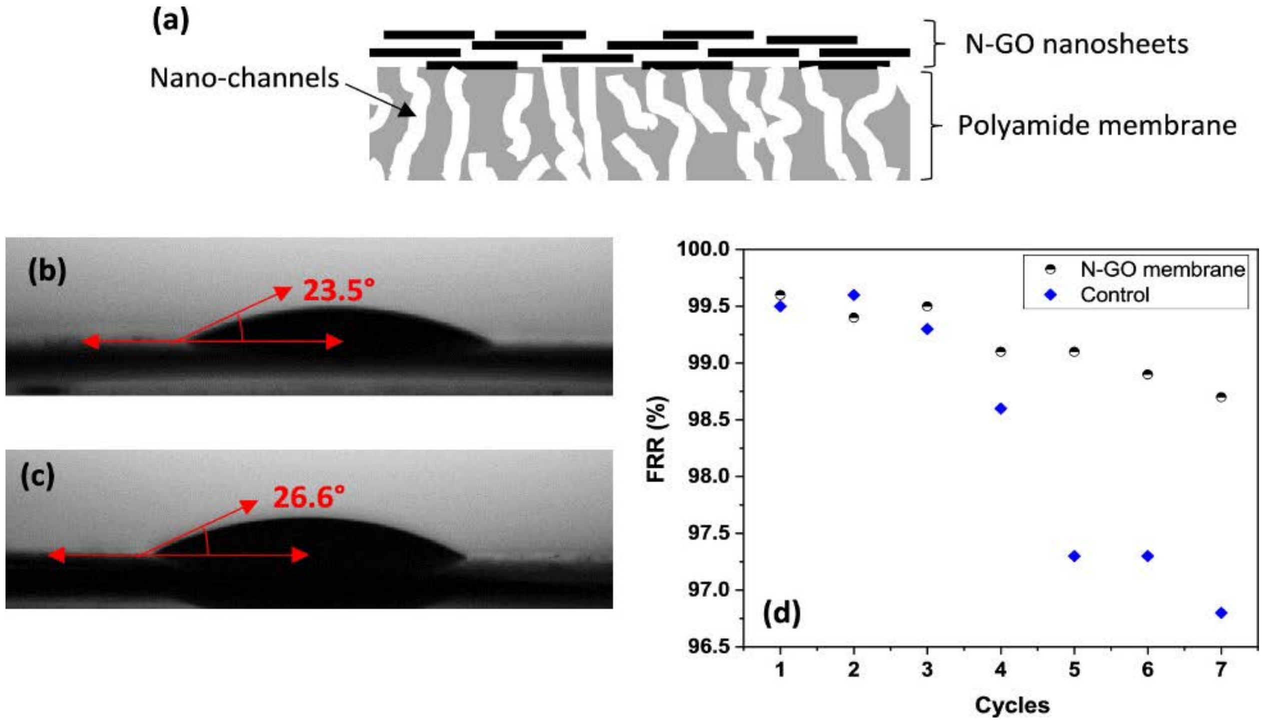
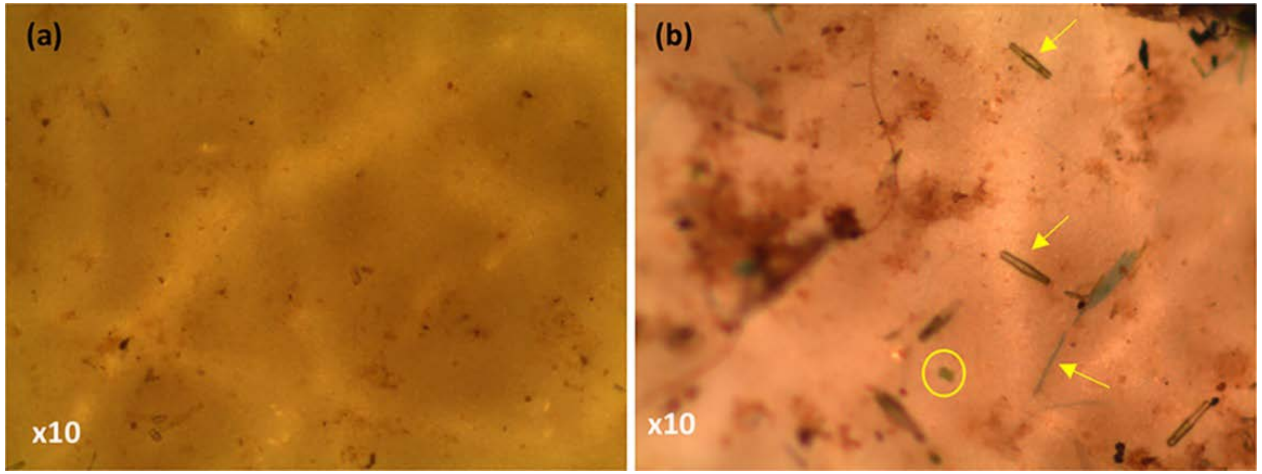


Water purification application

a) schematic presentation of the N-GO-coated-PA membrane,
b) water contact angle of the control and
c) WCA of N-GO-coated-PA membranes
d) higher flux recovery ratio against the number of water filtration cycles.



Microscopic images showing the degree of algal growth on (a) N-GO-coated and (b) control polyamide membranes

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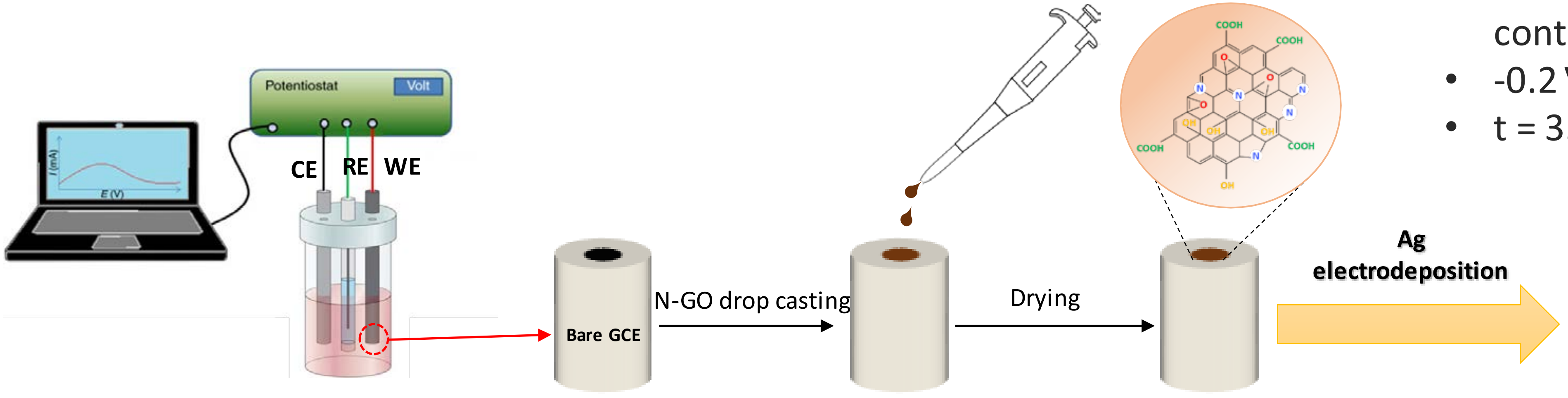
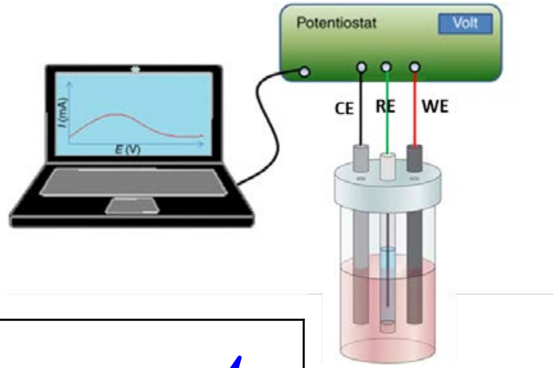
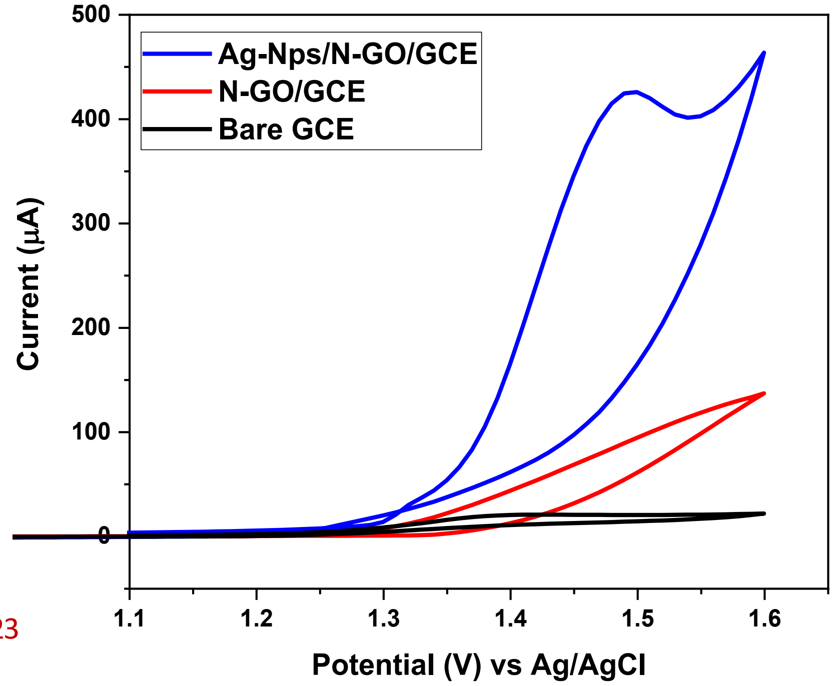
Microwave Plasma: N-Graphene Oxide Oxalic Acid Sensor

- 1 mM KNO_3 solution containing 0.1 mM $AgNO_3$
- -0.2 V potential
- t = 350 sec





- Excessive consumption of oxalic acid can cause
  - kidney stones
  - Disturbance in heart and nervous system
- USDA recommended 9.7 mg in 1 g intake



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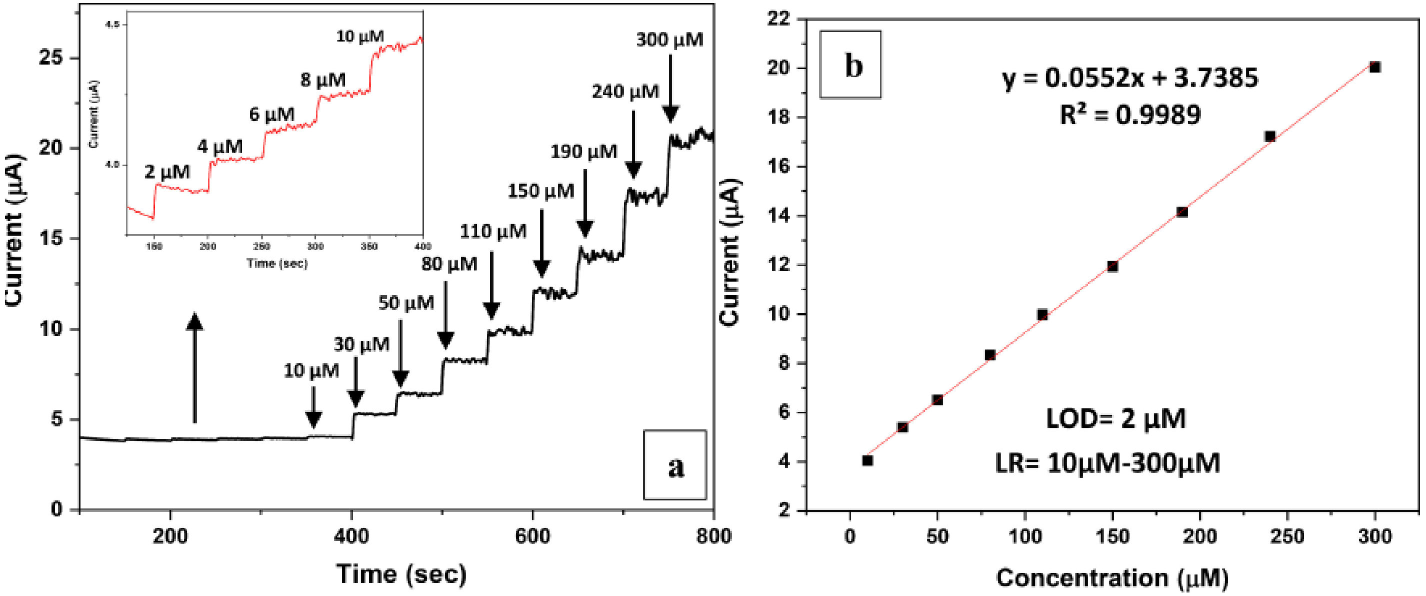
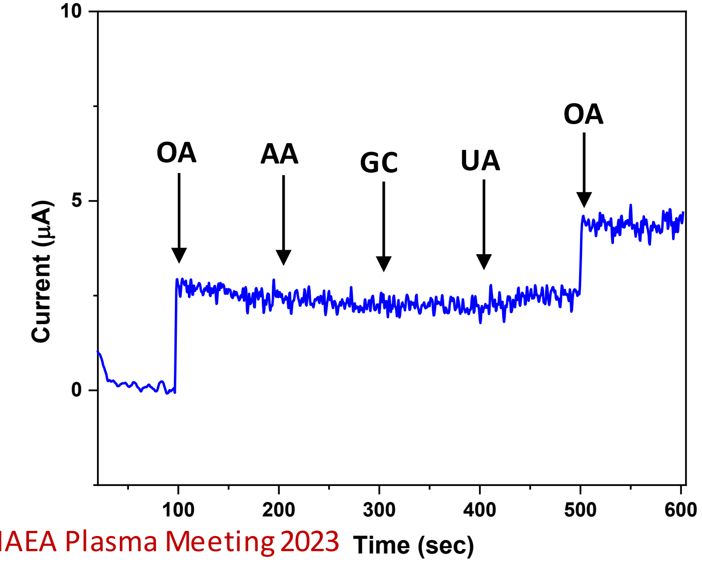
Microwave Plasma: N-Graphene Oxide from Aniline

Electrochemical sensor: oxalic acid detection

Amperometric response of the Ag-Nps/N-GO/GCE in stirred 0.1 M PBS with sequential injections of OA at 1.2 V potential (b) Calibration curve showing OA current response against its concentration.



Amperometric response of Ag-Nps/N-GO/GCE towards OA (50 µM), ascorbic acid (100 µM), glucose (50 µM) and uric acid (100 µM) in 0.1 M PBS at 1.2 V



Zafar, M. A., Varghese, O. K., Robles Hernandez, F. C., Liu, Y., & Jacob, M. V. (2022). Single-Step Synthesis of Nitrogen-Doped Graphene Oxide from Aniline at Ambient Conditions. ACS Applied Materials & Interfaces.

Microwave Plasma: N-Graphene Oxide from Aniline

Comparison

	Our method	Conventional methods
Processing environment	Ambient air	HEATING
Precursor materials	Single precursor, no toxic gases	Hazardous & expensive gases
Processing duration	Short	Long
Process Design	Simple (single step)	Complex (multi-staged)
	80 W (90 % cheaper)	2 kW Expensive

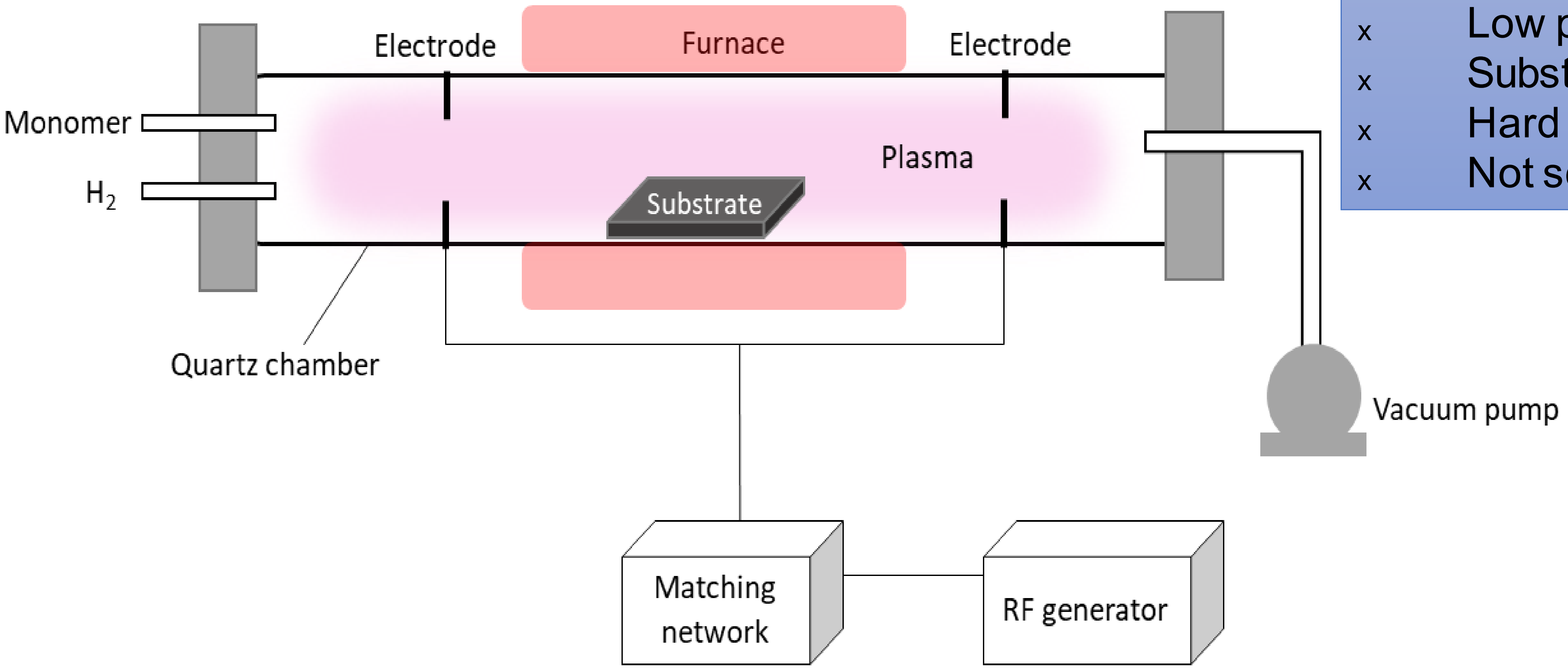
Zafar, M. A., Varghese, O. K., Robles Hernandez, F. C., Liu, Y., & Jacob, M. V. (2022). Single-Step Synthesis of Nitrogen-Doped Graphene Oxide from Aniline at Ambient Conditions. ACS Applied Materials & Interfaces.

RF Plasma-Enhanced Chemical Vapour Deposition

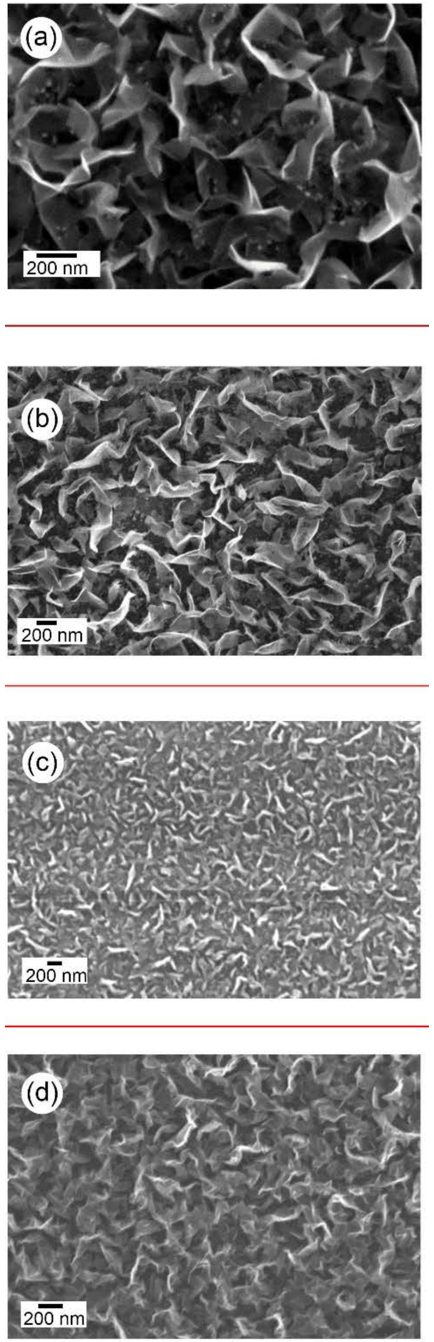
- The RF signal is used to setup a time varying electric field between the plasma and the electrode
- This electric field accelerates the electrons in and out of the plasma
- The electrons gain energy and ionize the local gas

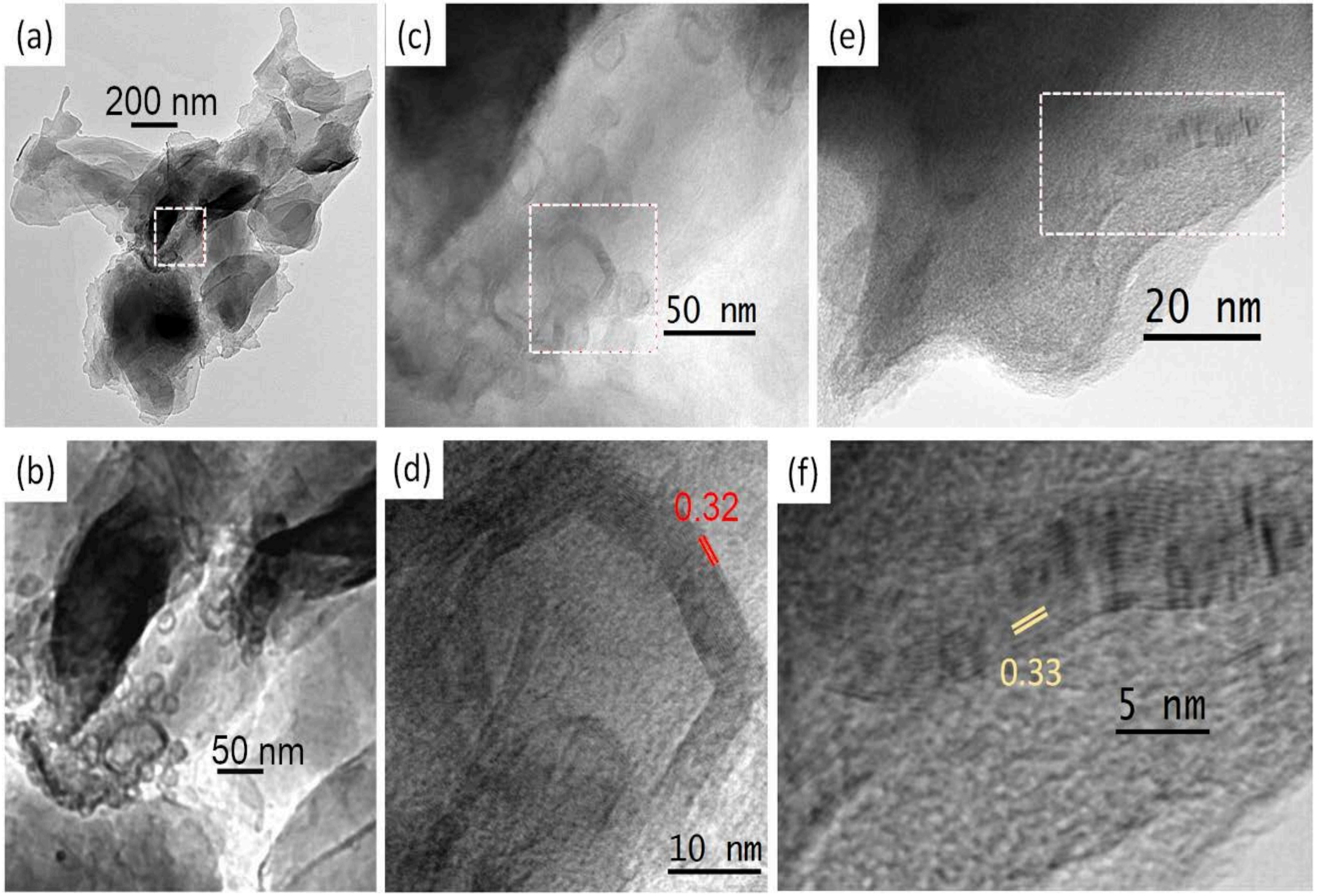
✓ Can achieve mono layer graphene
✓ Requires low temperature

x Requires precise parameters control
x Pre-heating
x Low productivity
x Substrate is must
x Hard to transfer
x Not scalable



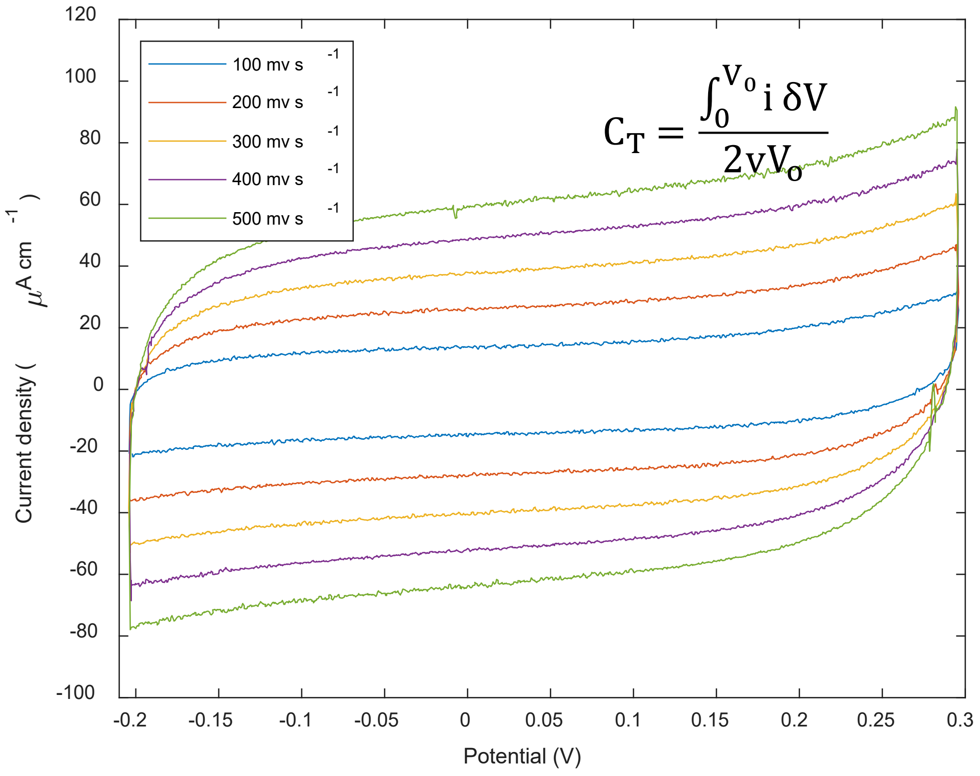
RF Plasma: Catalyst Free Graphene Nano-onions Fabrication

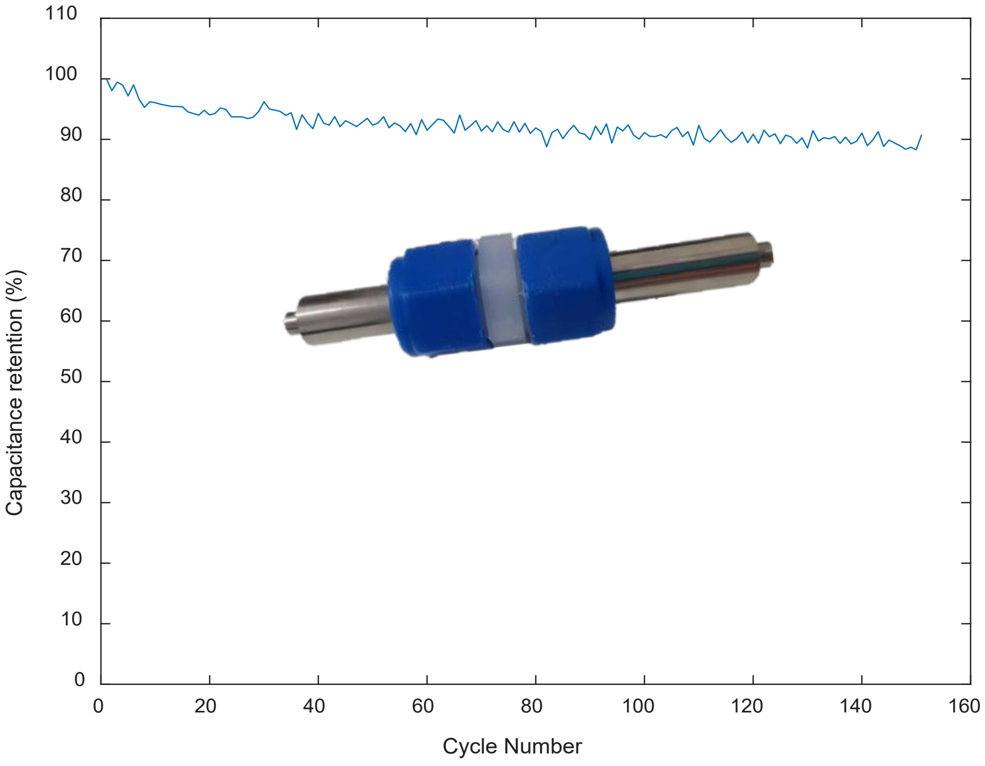




Surjith Alancherry et al, Applied Materials and Interface, 2020, 2(26):29594-29604, Fabrication of Nano-Onion-Structured Graphene Films from Citrus sinensis Extract

RF Plasma: Cyclic Voltammetry of Graphene



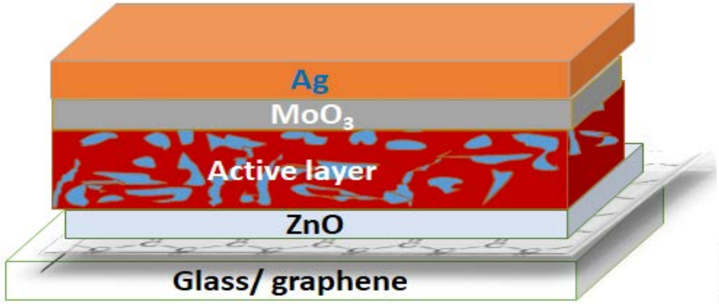


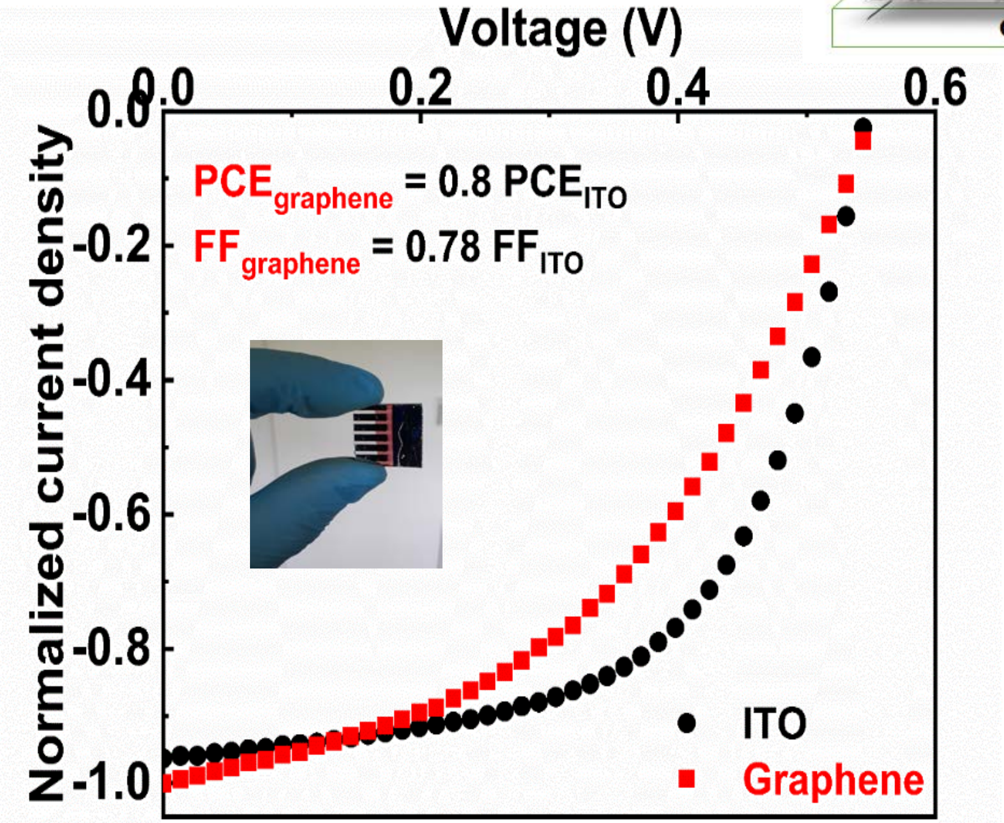
Capacitance = 140µF per cm^2

630 F per device

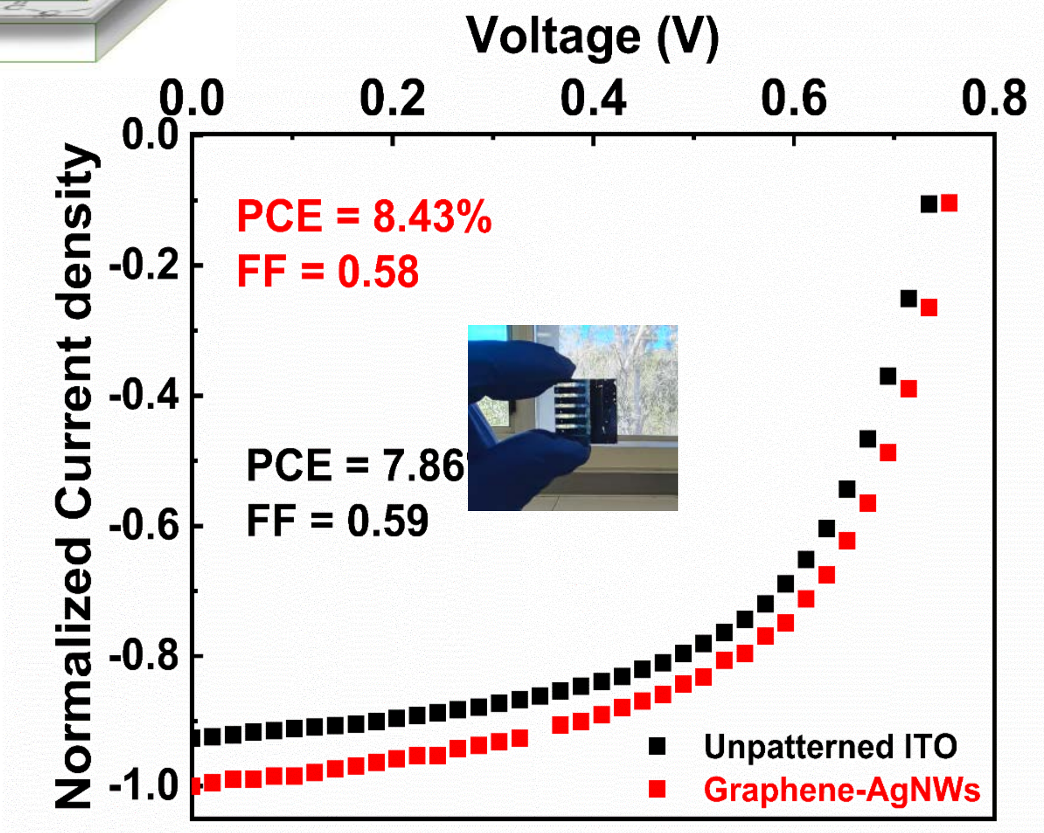
Surjith Alancherry et al, Applied Materials and Interface, 2020, 2(26):29594-29604, Fabrication of Nano-Onion-Structured Graphene Films from Citrus sinensis Extract

RF Plasma: J-V characteristics for graphene-based OPVs





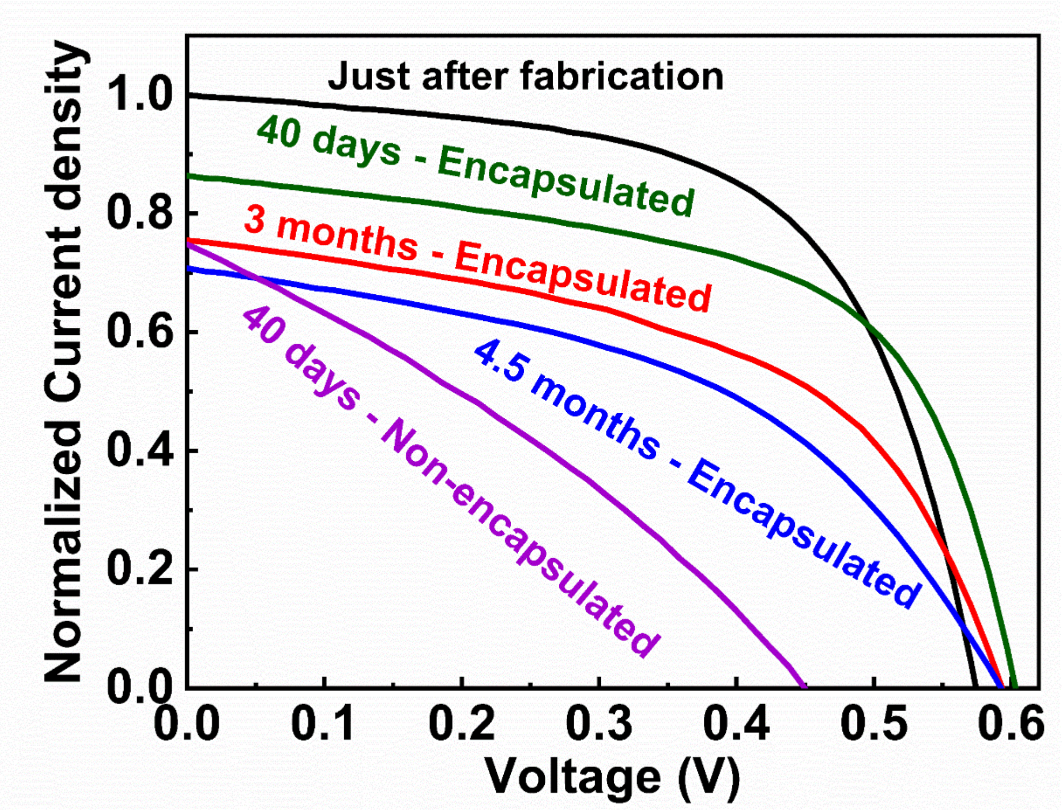
TCE/ZnO/P3HT: $PC_{70}BM$/MoO3/Ag

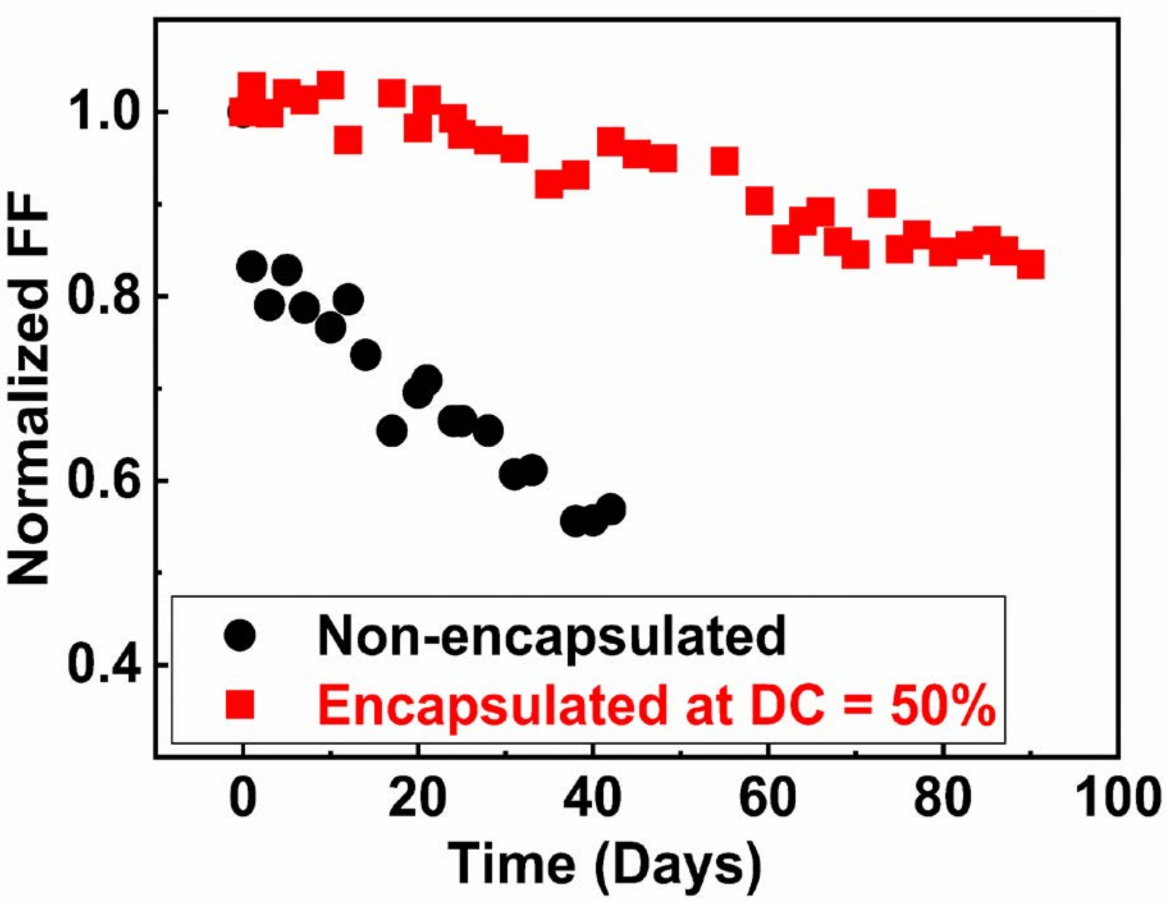


TCE/ZnO/PM6: Y6/MoO3/Ag

Kamel, Michael SA, Michael Oelgemöller, and Mohan V. Jacob. "Sustainable plasma polymer encapsulation materials for organic solar cells." Journal of Materials Chemistry A 10.9 (2022): 4683-4694.

RF Plasma: Effect of pp-encapsulation on device stability





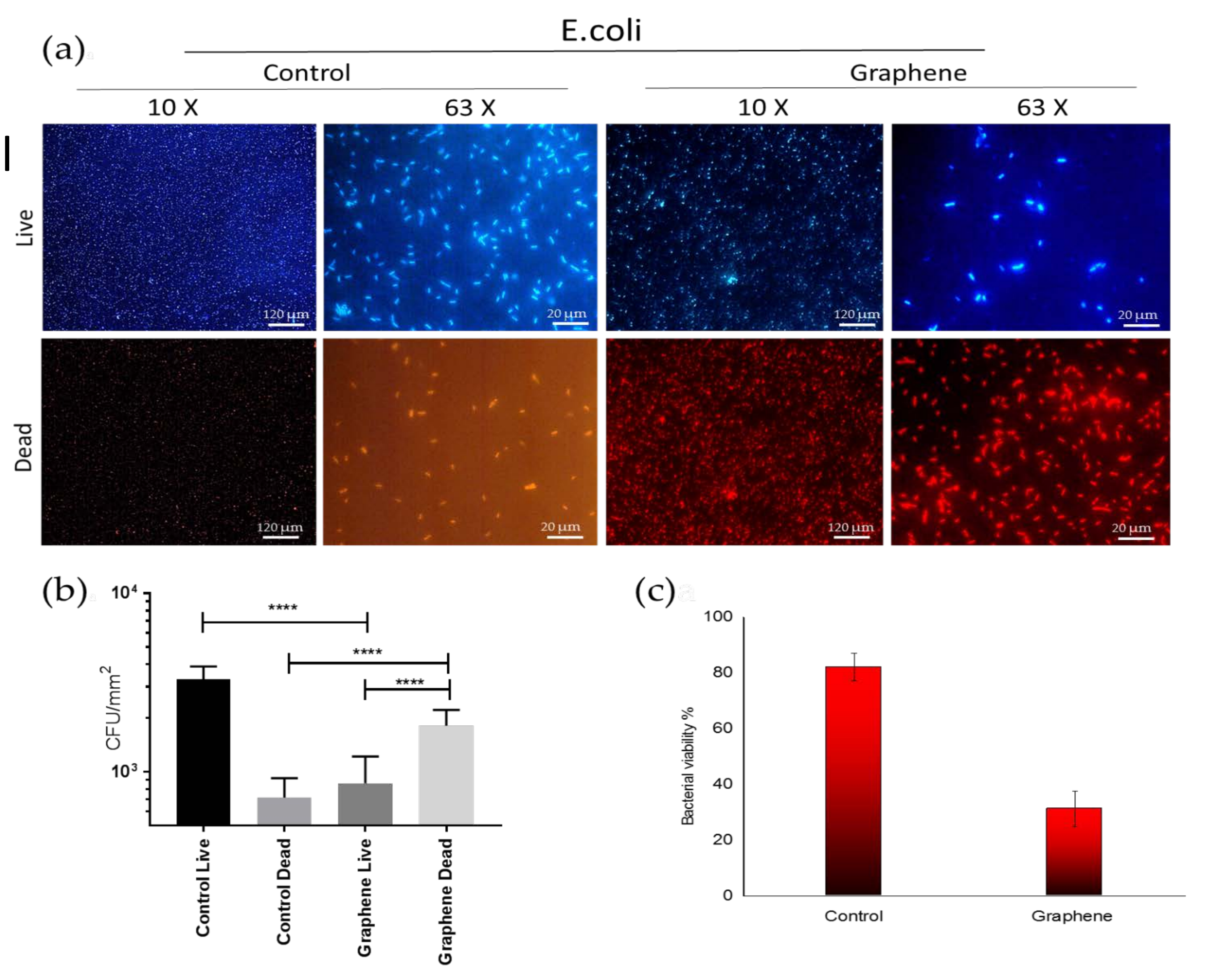
	960 h	2160 h	3240 h
Non-encapsulated	Degraded		
Encapsulated	PCE = 0.9 PCE_i	0.66 PCE_i	0.57 PCE_i
(i) refers to initial	FF = 0.98 FF_i	0.87 FF_i	0.78 FF_i
	V_{OC}		Unchanged

Kamel, Michael SA, Michael Oelgemöller, and Mohan V. Jacob. "Sustainable plasma polymer encapsulation materials for organic solar cells." Journal of Materials Chemistry A 10.9 (2022): 4683-4694.

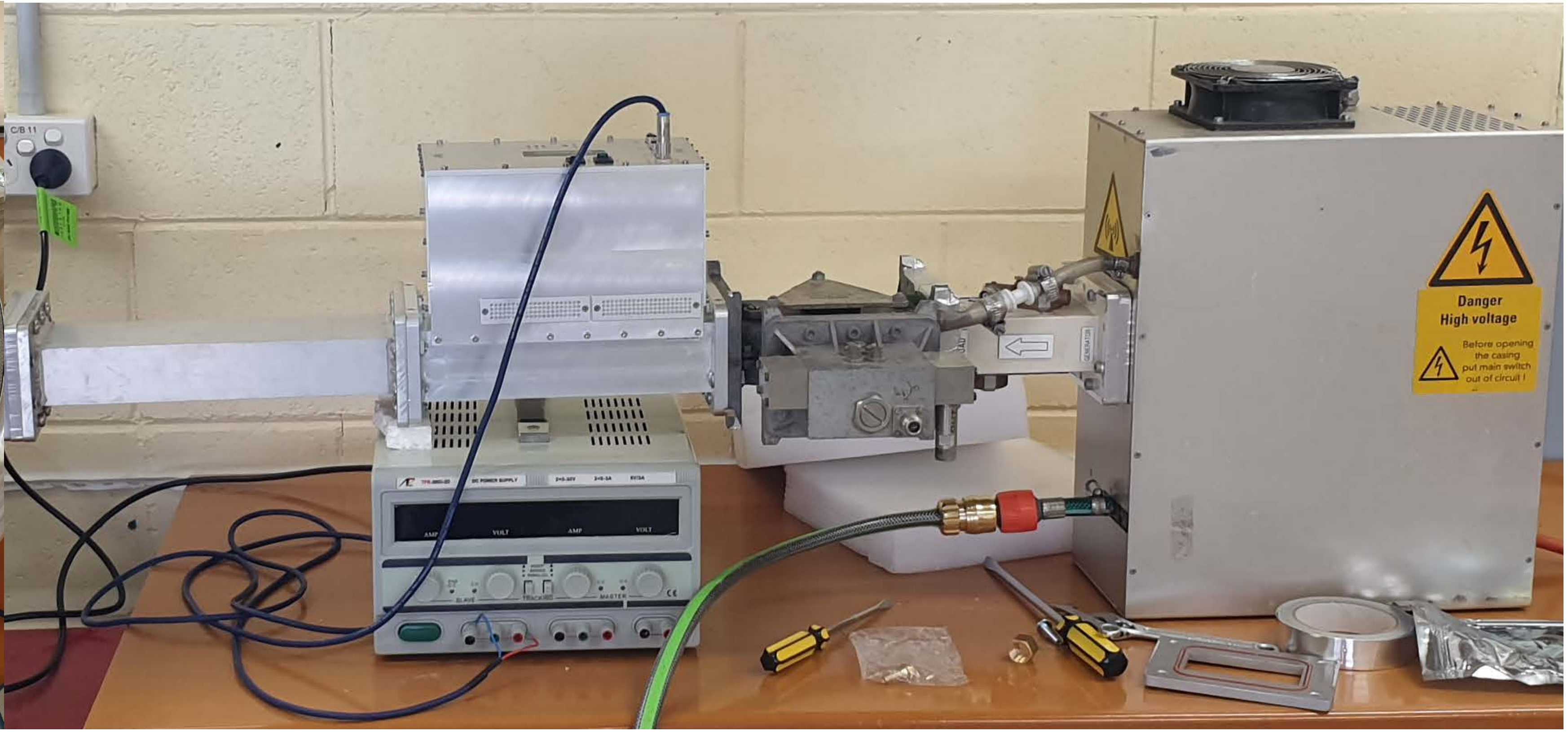
RF Plasma: Graphene: Antibacterial Properties

- An excellent antibacterial material but fabrication temperature may limit the applications
- Graphene can also be used as a compound with silver nanoparticles to increase antibacterial properties even further.

Al-Jumaili, Ahmed, et al. "Bactericidal vertically aligned graphene networks derived from renewable precursor." Carbon Trends 7 (2022): 100157.



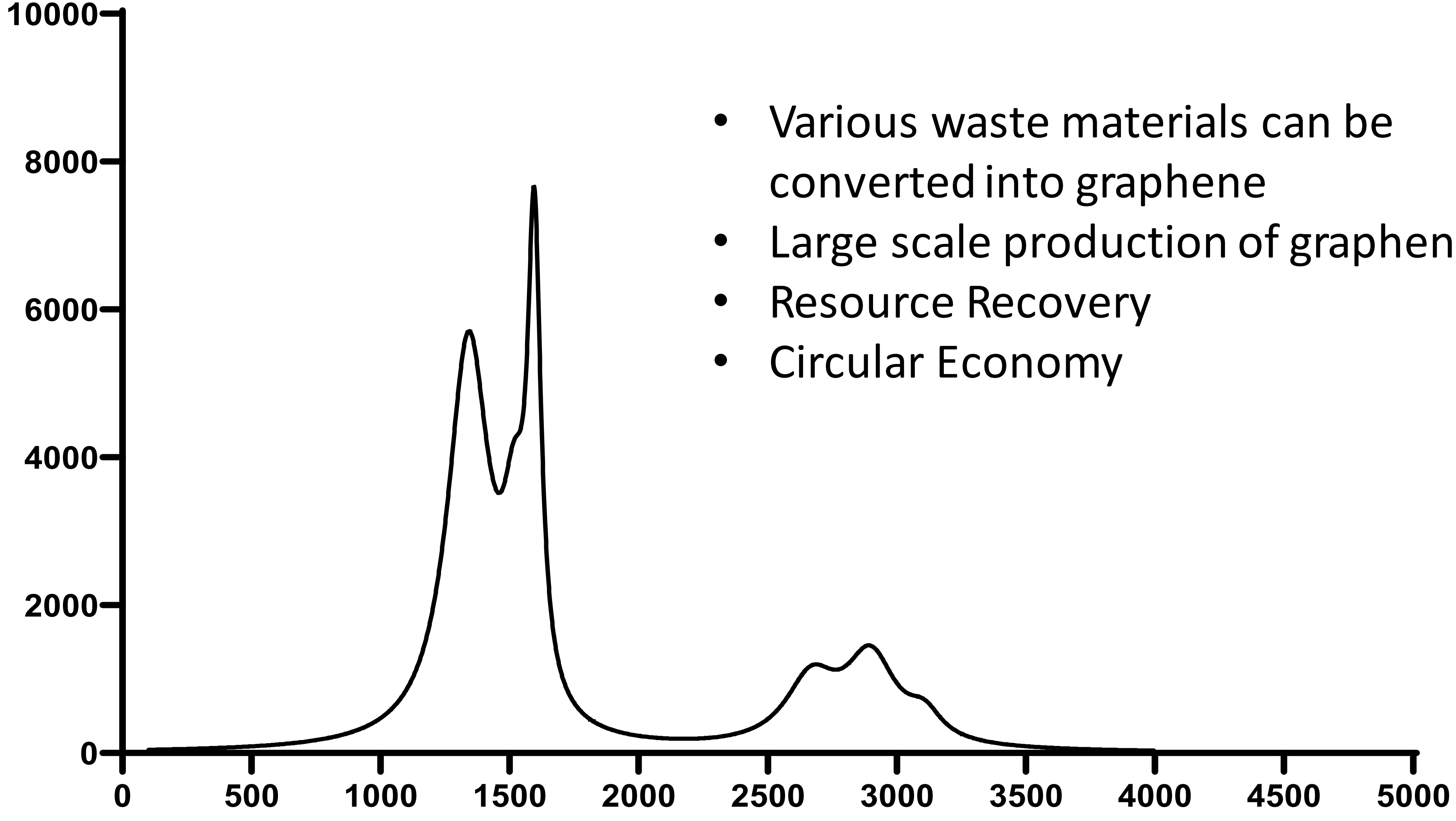
Microwave Assisted Pyrolysis for Waste to Resources



By-products ➡

- Bio-gas (CO_2, CH_4, H_2, N_2)
- Bio-oil
- Bio-char (rich in Carbon)

Microwave Assisted Pyrolysis: Waste to Resources



- Various waste materials can be converted into graphene
- Large scale production of graphene
- Resource Recovery
- Circular Economy

Allende, Scarlett, Graham Brodie, and Mohan V. Jacob. "Energy recovery from sugarcane bagasse under varying microwave-assisted pyrolysis conditions." Bioresource Technology Reports 20 (2022): 101283.

Opportunities:
Pyrolysis in conjunction with Plasma Technology for Waste to Resources

Waste Materials (Plastic, Agricultural Waste, Food Waste etc): $0

Microwave Assisted Pyrolysis

Byproducts

- ✓ Gas → Microwave Plasma
- × Oil
- ✓ Char → Microwave Plasma

Microwave Plasma → Graphene

Fast Production
Bulk Production
No Environmental hazards

Graphene → **Applications**

- ✓ Sensor
- ✓ Storage (Battery)
- ✓ Concrete
- ✓ Water Purification

1Kg ($0) waste – converted to 10 gm graphene ($100)

50kg waste/ day → $5,000

Conclusions

Plasma for nanomaterials	**Plasma (RF and Microwave) is excellent tool for the sustainable synthesis of Graphene or nanomaterials**
Past vs present	**Graphene synthesis is complex and time-consuming, involving high temperatures, vacuum requirements, and material transfer etc. Plasma based synthesis simplified and accelerated this process**
Future	**Microwave plasma could simplify large-scale graphene production and could also covert waste into resources**
Applications	**Plasma could assist the development of sustainable materials for electronics, sensors, storage, membrane, biomedical applications**

JCU

Thankyou very much for your attention

Email: Mohan.Jacob@jcu.edu.au