Synthesis of nitrogen doped graphene derivatives for new renewable nano structured membranes used for direct alkaline ethanol fuel cell

Azadeh Motealleh

PhD in Material Science

Abalonyx
Innovative materials

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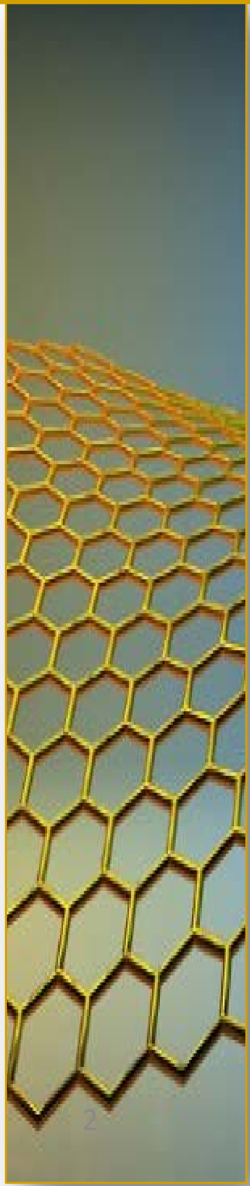
Outline

- **Abalonyx AS**
- **NanoElMem project**
- **Nitrogen Doping**
- **Results and Discussion**
- **Summary**



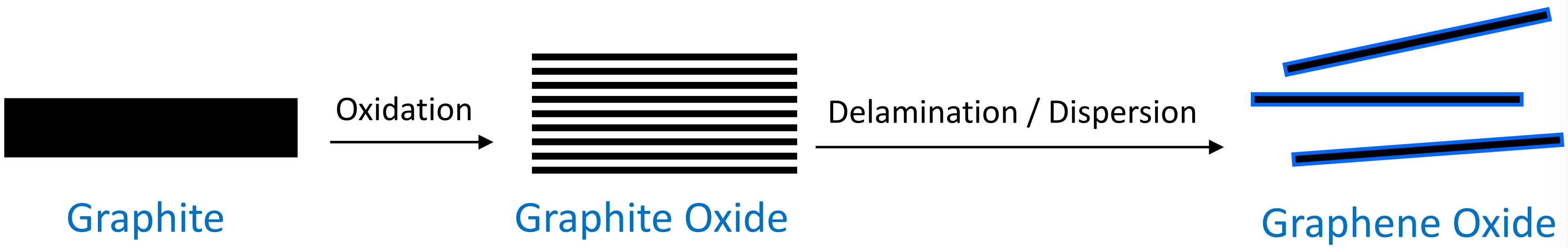
Location

Labs and offices at
Sintef, Oslo, Norway

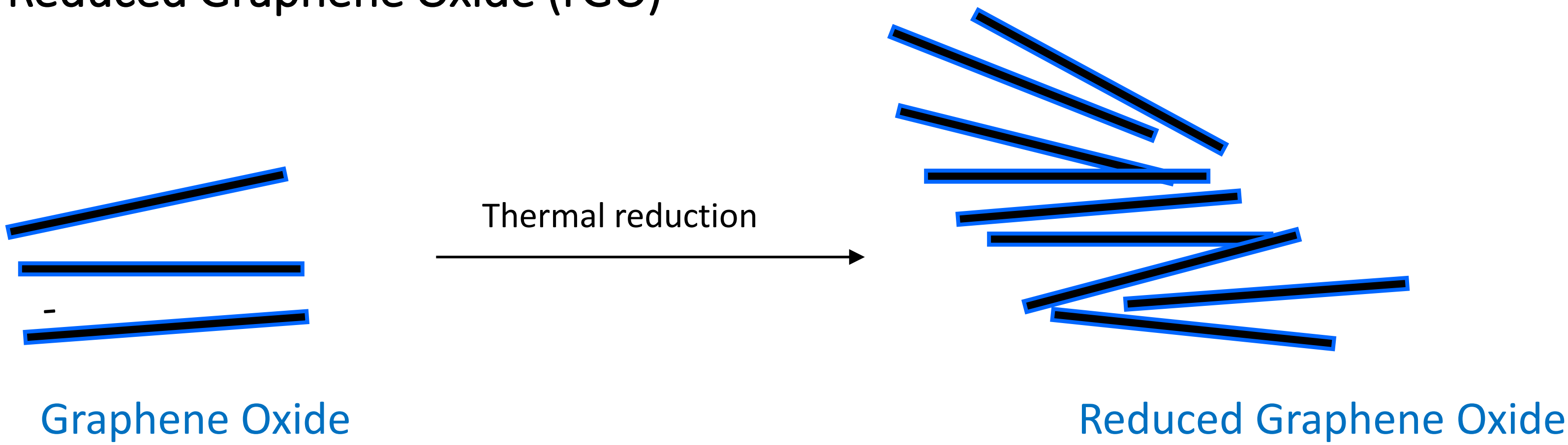
Production site at
Tofte, Norway

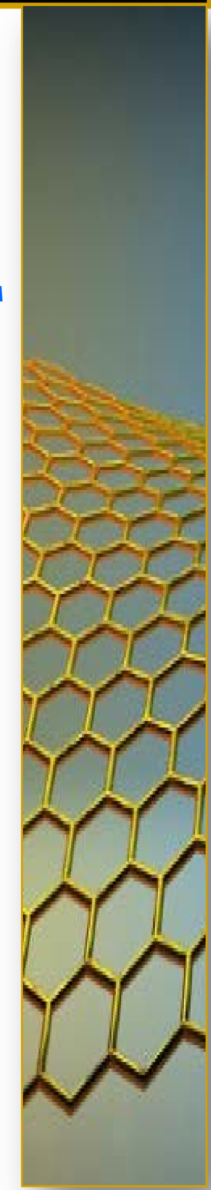
Products

Graphene Oxide (GO)



Reduced Graphene Oxide (rGO)

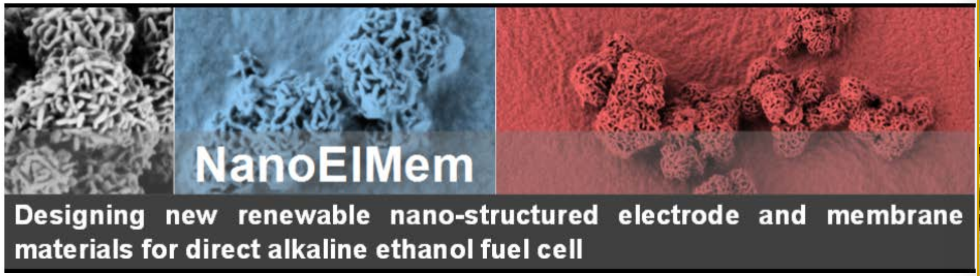




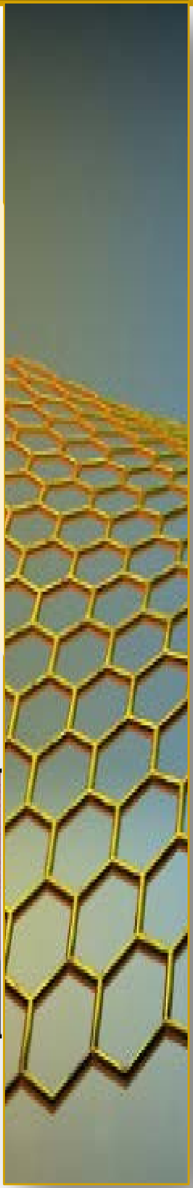
Participation in EU projects

- NanoElMem

Designing new renewable **nano-structured electrode** and **membrane** materials for direct alkaline ethanol **fuel cell**



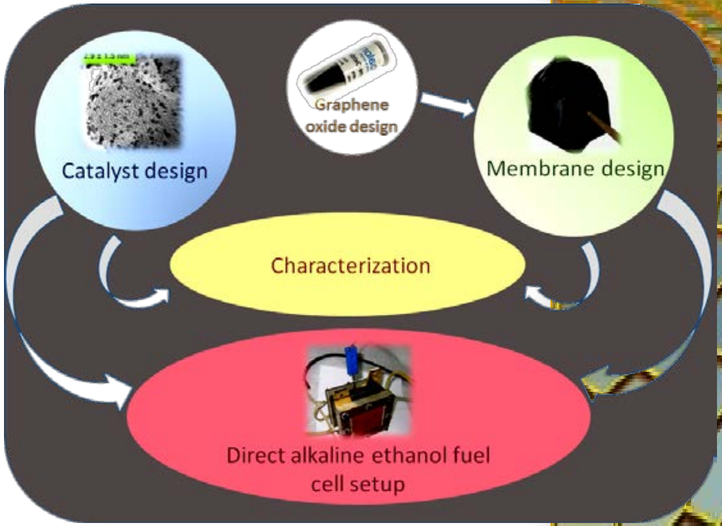
M-era.Net **Funded in 2017**



NanoElMem Partners

Coordinator (P1): University of Maribor (UM)	Partner 2: University of Nova Gorica (UNG)	Partner 3: Abalonyx	Partner 4: Norwegian University of Science & Technology (NTNU)	Partner 5: Chang Gung University (CGU)
Slovenia	Slovenia	Norway	Norway	Taiwan

- **Emphasis on :**
- **Platinum (Pt)-free anode catalysts**
- **Nano-composite membranes**

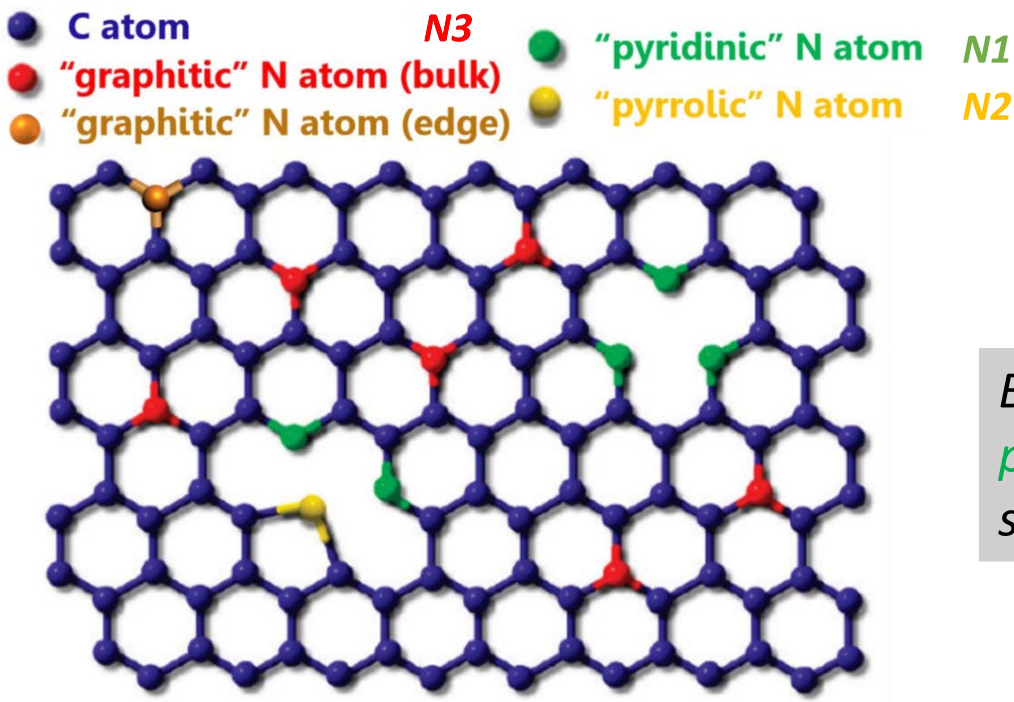


Abalonyx + University of Maribor

Nitrogen Doping

The introduction of N into graphene can modify the local electronic structure.

0.6 at% of N doping → 4 times higher electrical conductivity

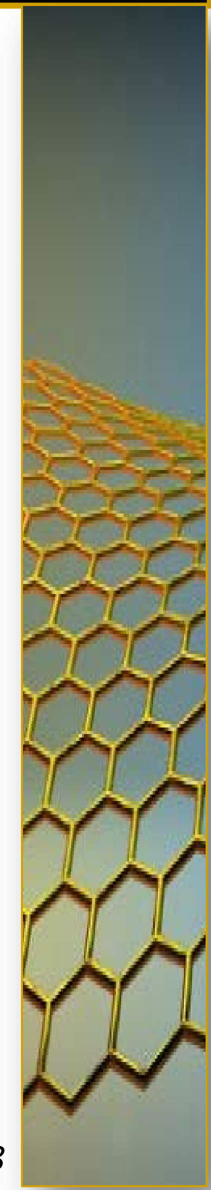


N bonding Configurations

*Both graphitic (N3) and pyridinic (N1) have been suggested to facilitate ORR**

*oxygen reduction reaction

Wei et. Al. Nano Lett. ***2009****, 9, 1752–1758*



Results and Discussion
(Synthesis)

N doped GO

GO

NH3

- **1- Ultrasonic treatment**

  A simple, rapid and scalable wet-chemical method

  Parameters: **Time** and **Temperature**.

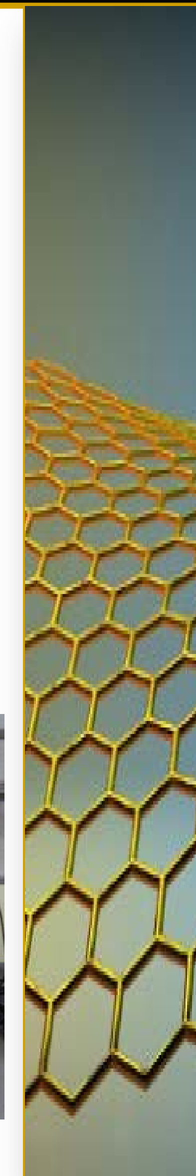
- **2- Plasma treatment**

  Exposure to NH_3 gas at room temp

  Parameters: **Exposure time** and **Plasma strength**

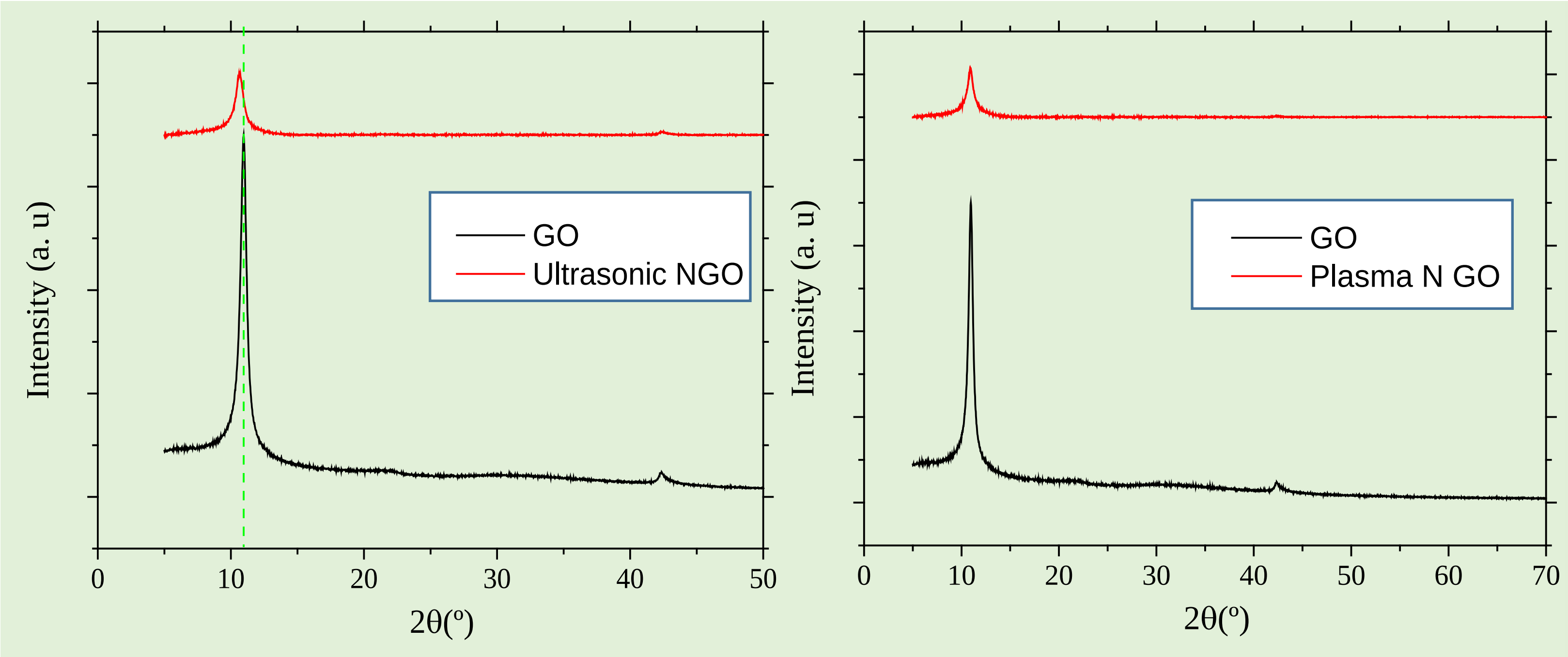
Plasma Reactor

www.haydale.com

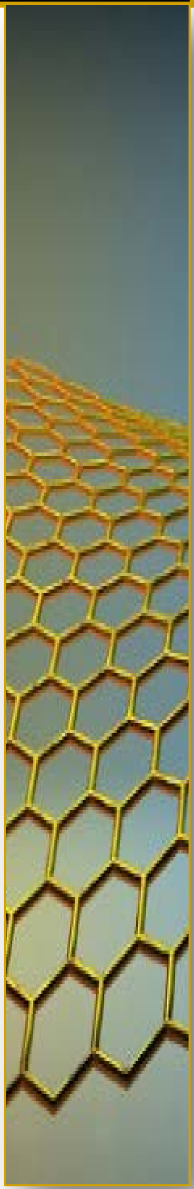


Results and Discussion (Characterizations)

X-ray diffractometry (XRD)

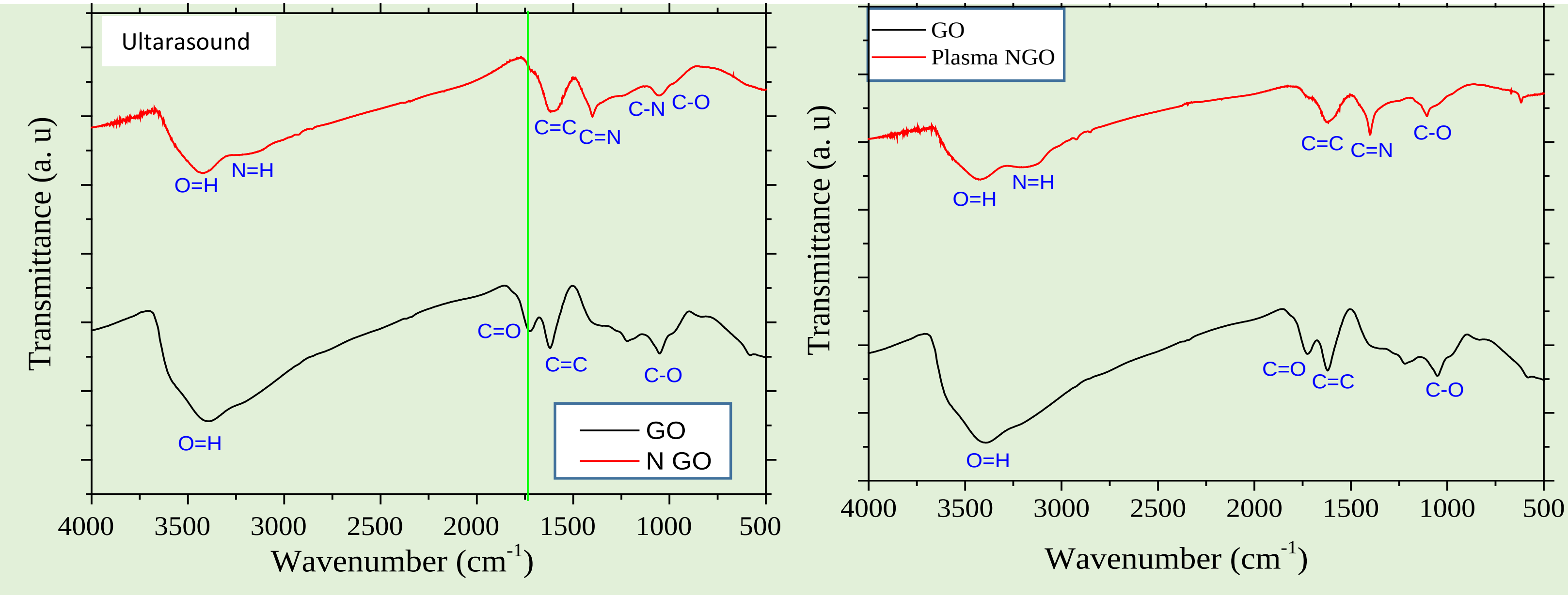


- GO peak at around 11°
- NGO peak with a slight downshift
- Expansion of an interlayer distance as a result of insertion of N atoms



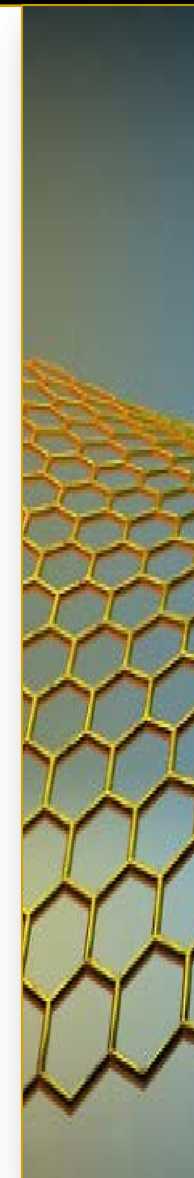
Results and Discussion (Characterizations)

Fourier transform infrared (FTIR)



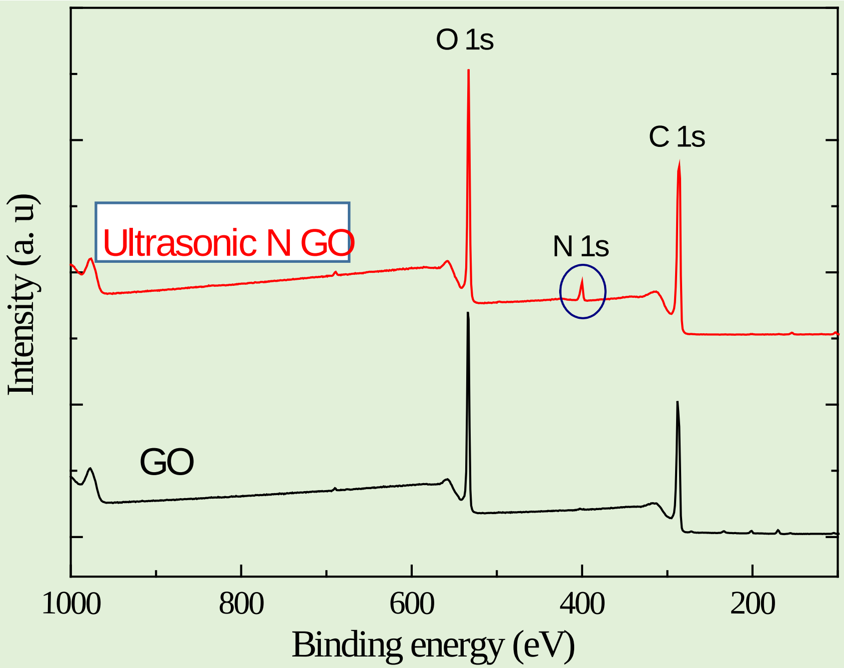
GO: The peaks at around 1722, 1618, and 1055 cm^{-1} correspond to the stretching vibrations of C=O, C=C, and C–O groups.

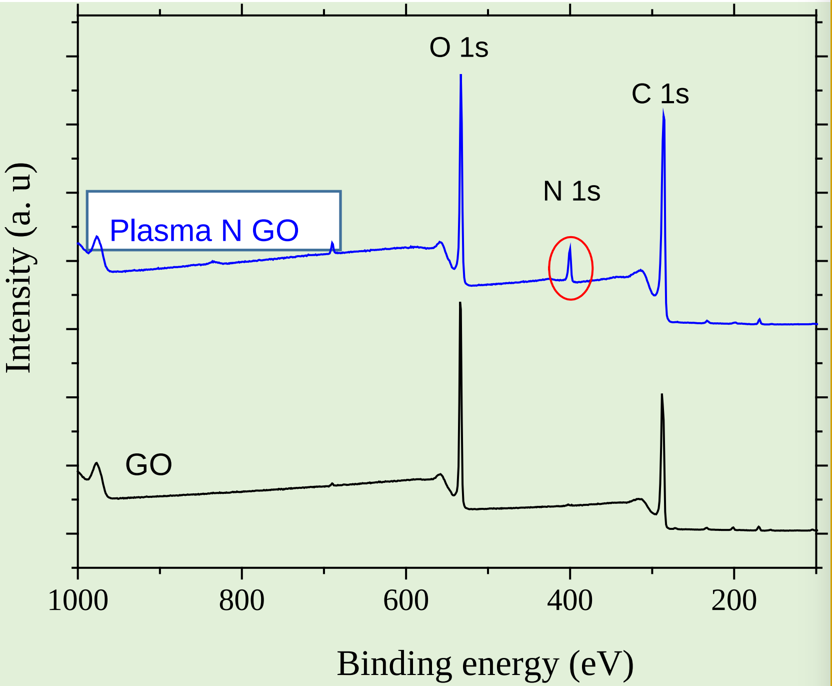
NGO: The intensity of the C=O peak significantly reduced and meanwhile, two new bands at about **1400** and **1250** cm^{-1} appeared that originated from C=N and C–N stretching vibrations, respectively.



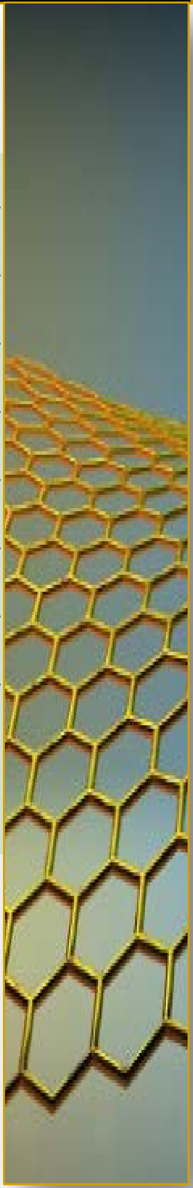
Results and Discussion (Characterizations)

X-ray photoelectron spectroscopy (XPS)





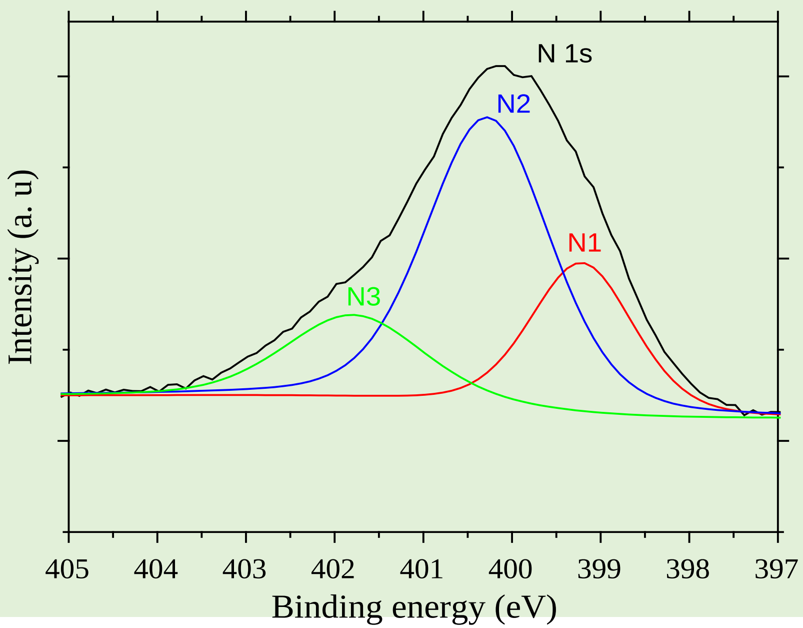
The wide-survey spectra shows presence of N in addition to C and O after doping in NGO samples.



Results and Discussion (Characterizations)

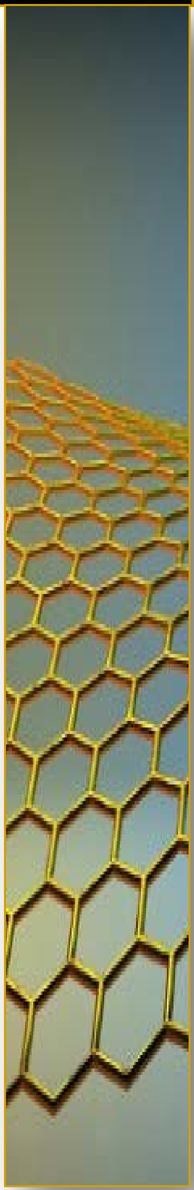
XPS Calculations

Sample	C (at.%)	O (at.%)	N (a.%)
GO	66.79	30.89	0.3
Ultrasonic NGO	72.94	23.62	3.44
Plasma NGO	74.68	19.91	5.41



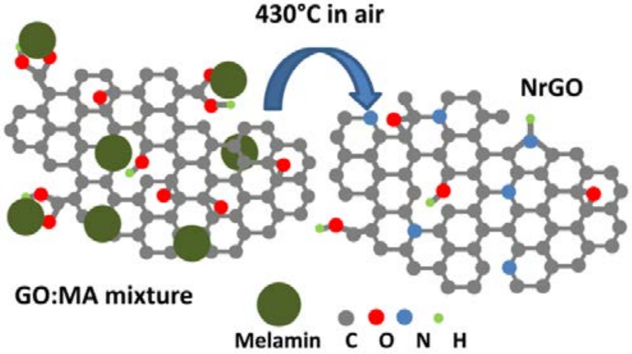
Around **50% of N** belongs to **pyridinic** (N1) and **graphitic** (N3) that facilitate oxygen reduction reaction (ORR).

N configuration	% in total N	Amount in at.%
N1 (pyridinic)	28.16	1.03
N2 (pyrrolic)	51.46	1.9
N3 (graphitic)	20.38	0.75



Results and Discussion
(Synthesis)

N doped rGO



- **1- Thermal annealing**

The **annealing temperature** and the **nature of the N sources (precursors).**

Melamine (MA) used as N precursor with different ratios
Heat treated at 450°C and at 900°C

- **2- Plasma treatment**

Exposure to NH_3 gas at room temp

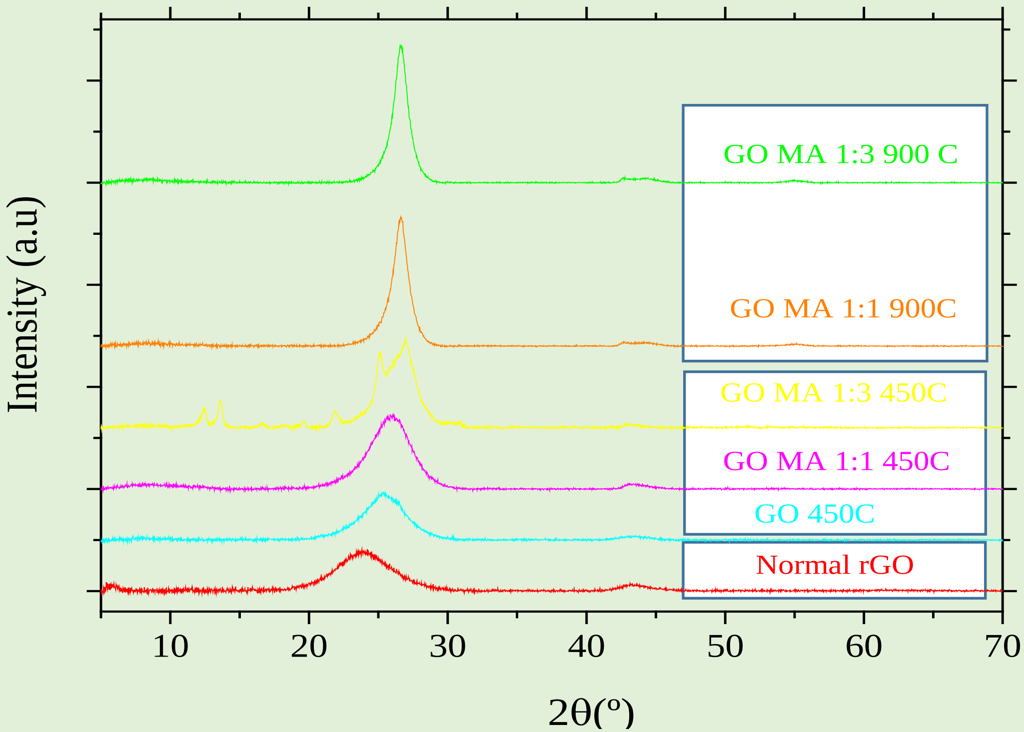
Parameters: **Exposure time** and **Plasma strength**

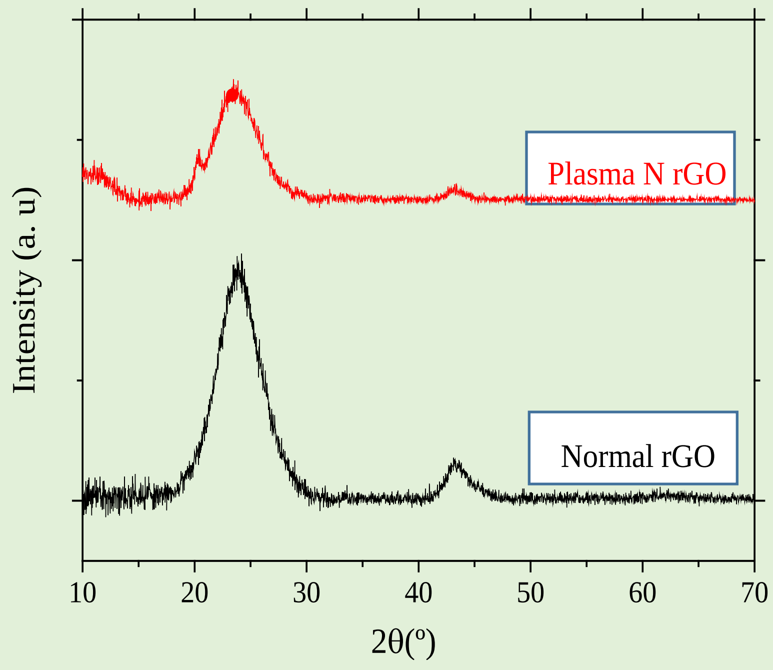
Plasma Reactor

www.haydale.com

Results and Discussion (Characterizations)

X-ray diffractometry (XRD)



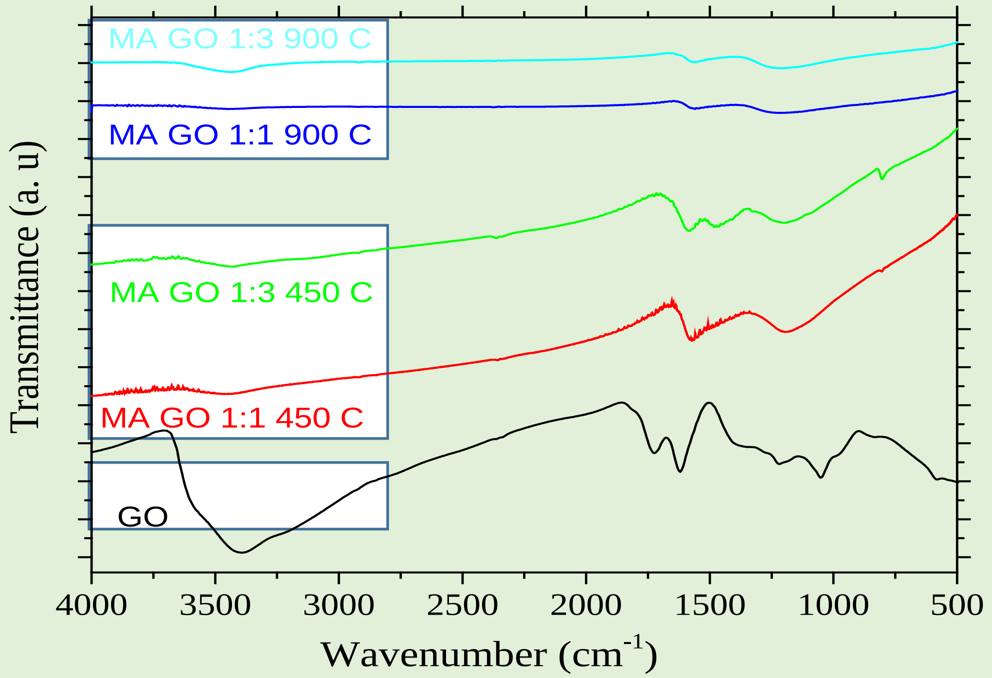


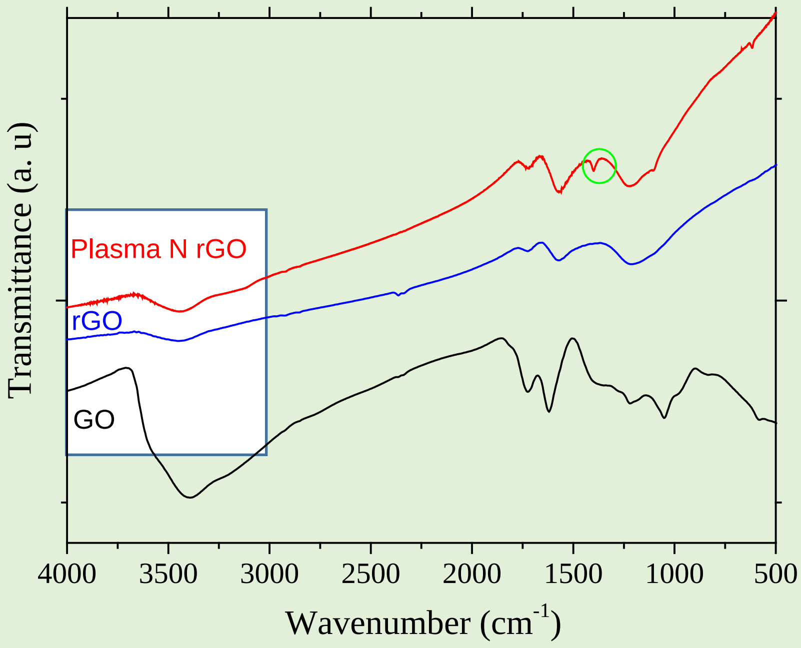
The degree of crystallinity (peak intensity) of NrGO increases with increasing the temperature
The peak was shifted to a higher 2θ degree, implying a better reducibility.

Both rGO and NrGO show a broad peak placed at around 2θ = 24°.
The peak of NrGO show a broader width and weaker intensity.

Results and Discussion (Characterizations)

Fourier transform infrared (FTIR)

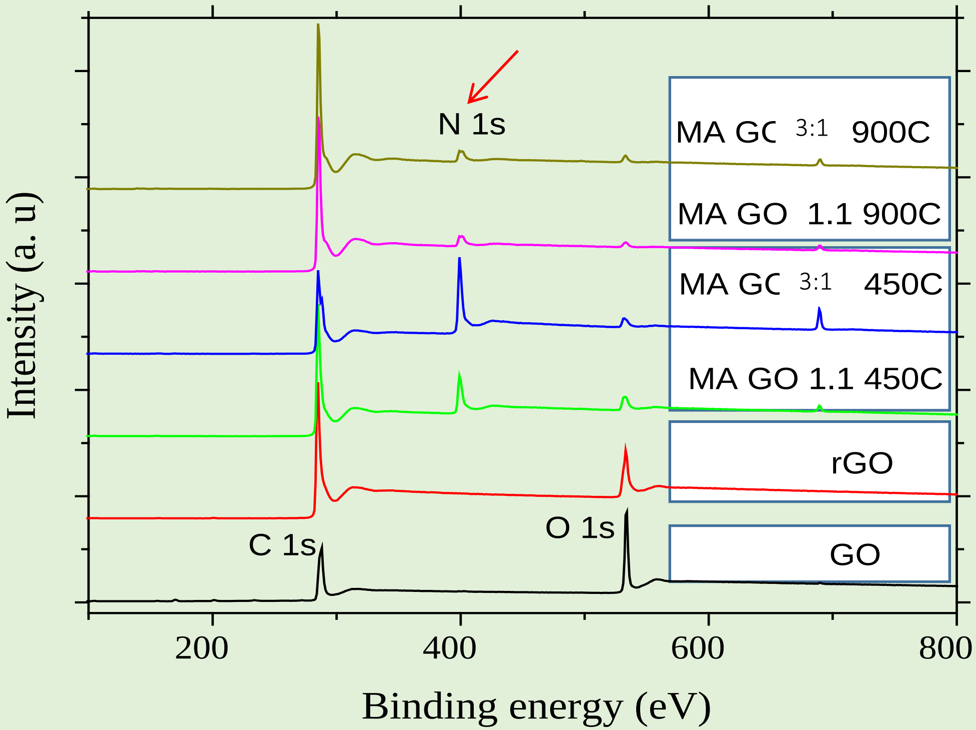


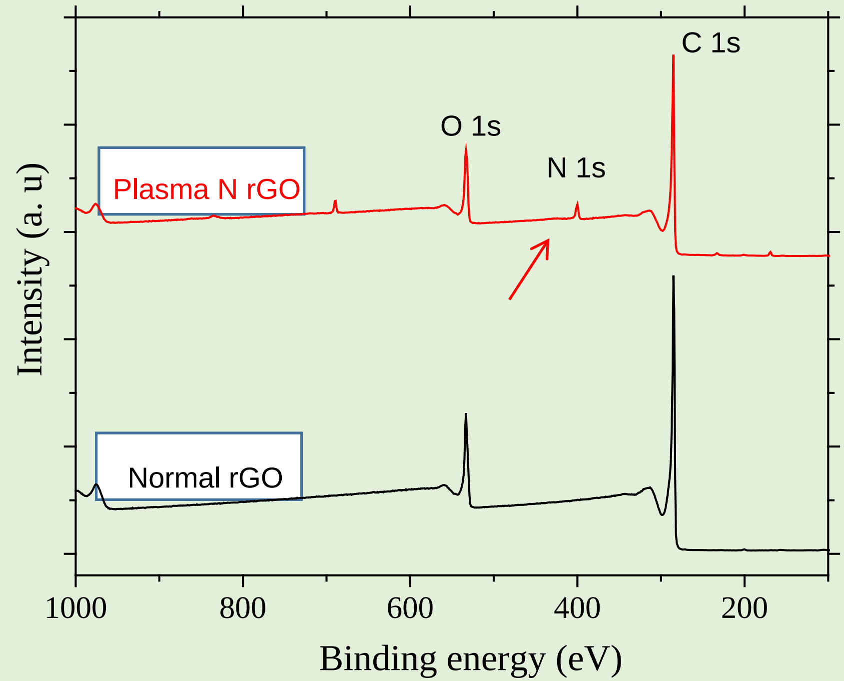


The peaks corresponding to the oxygen functionalities, such as the C–O and C=O, decreased dramatically. Two new bands at about **1400 and 1250 cm^{-1}** appeared that originated from **C=N and C–N**

Results and Discussion (Characterizations)

X-ray photoelectron spectroscopy (XPS)





The wide-survey spectra shows presence of N in addition to C and O after doping in NrGO samples.

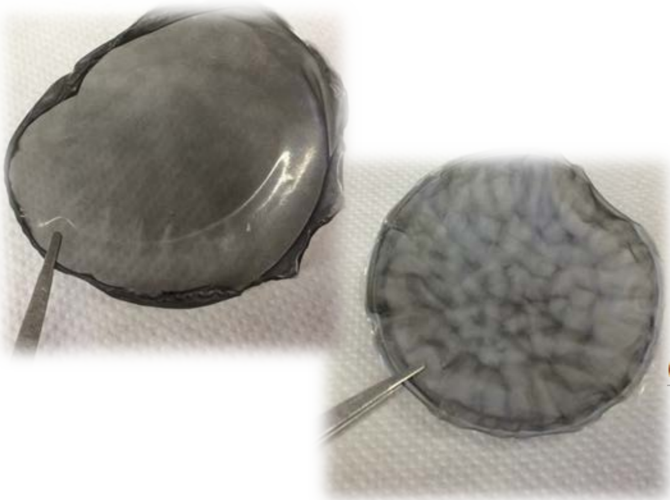
Results and Discussion (Characterizations)

XPS Calculations

Chemical Composition	C (at.%)	O(at.%)	N(at.%)
rGO	86.47	13.09	-
Plasma NrGO	82.94	13.58	3.47
MA GO 1:1 450°C	80.11	4.39	15.50
MA GO 3:1 450°C	67.69	2.95	29.34
MA GO 1:1 900°C	93.55	1.33	5.12
MA GO 3:1 900°C	92.63	1.77	5.60

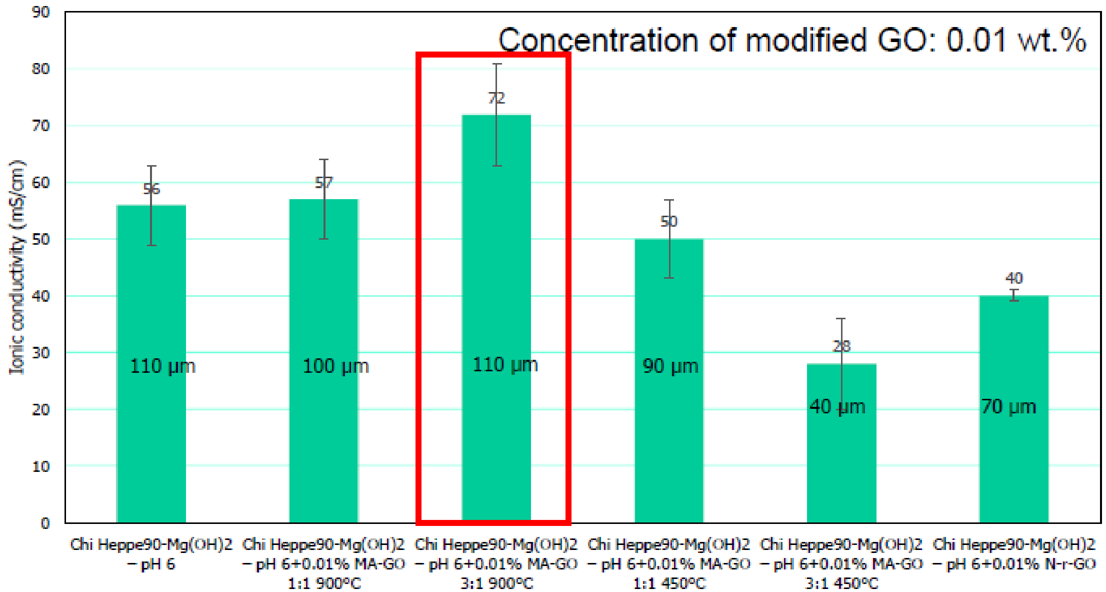
Chemical Composition	N1 %	N2 %	N3 %	N4 %	N(at.%)
NrGO Plasma	15.05	53.07	31.88	-	3.47
MA GO 1:1 450°C	39.7	33.6	21.7	4.95	15.50
MA GO 3:1 450°C	50.76	24.55	19.03	5.67	29.34
MA GO 1:1 900°C	31.88	40.17	14.48	13.47	5.12
MA GO 3:1 900°C	33.36	32.27	14.9	19.47	5.60

Composite membrane with NGO

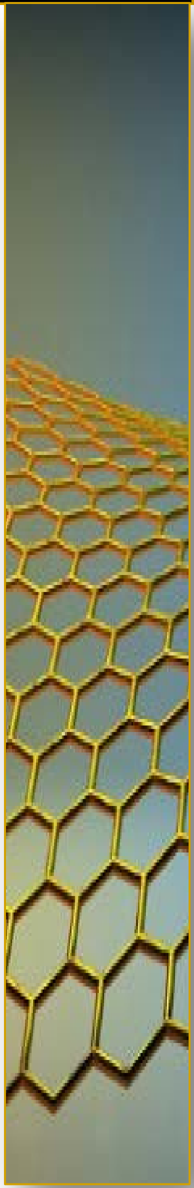


CS-90
0.01 % MA-GO (3:1, 900 °C)

OH – conductivity



Summary



- Abalonyx is producing GO and rGO in large scales.
- The energy section might be taught as a potential candidate for graphene commercialization.
- NanoElmem seeks for solutions to enhance performance of fuel cells by N doping of GO.

Abalonyx
Innovative materials

Azadeh Motealleh
am@abalonyx.no
Forskningsveien 1
0373 Oslo, Norway

Do you have any questions?

THANK YOU FOR YOUR ATTENTION !

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ACKNOWLEDGEMENTS

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EUROPEAN SCIENCE FOUNDATION

NanoElMem
Designing new renewable nano-structured electrode and membrane materials for direct alkaline ethanol fuel cell

MultiComp