Synthesis and Characterization of Polyaniline/Graphene Oxide Nancomposites

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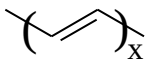
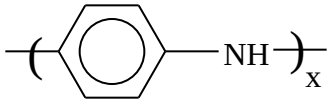
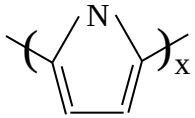
Intrinsically Conducting Polymers



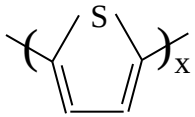
Polyacetylene (PAc)



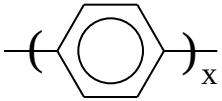
Polyaniline (PANI)



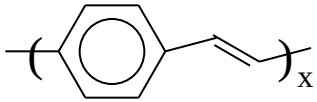
Polypyrrole (PPy)



Polythiophene (PTh)



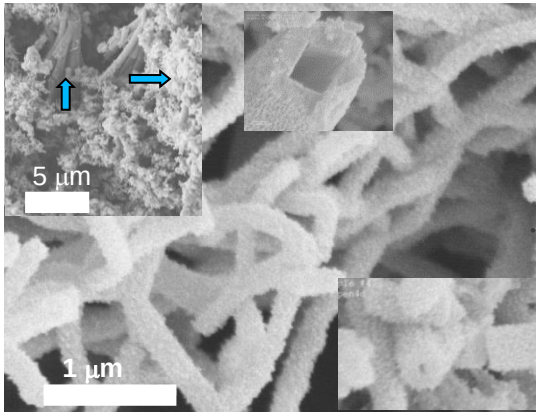
Poly(*p*-phenylene) (PPP)

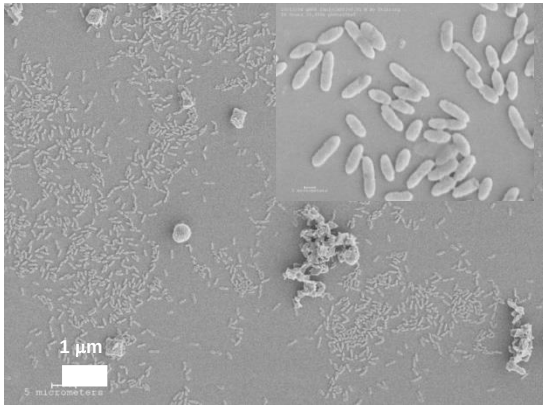


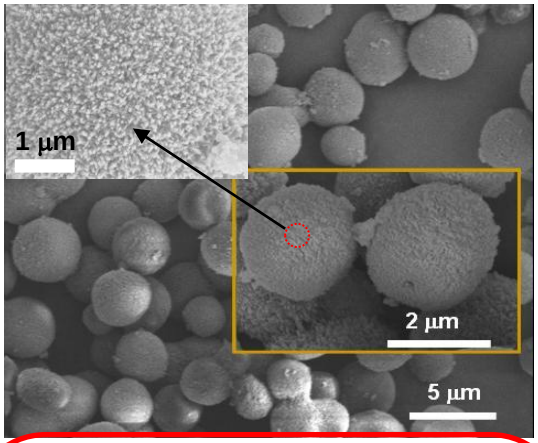
Poly(*p*-phenylene-vinylene) (PPV)

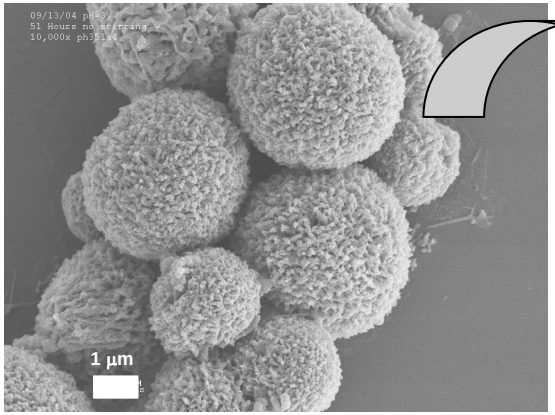
Key parameters*:

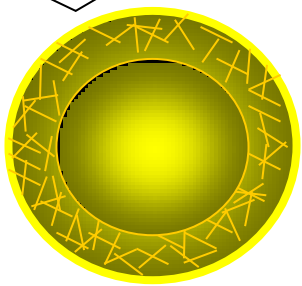
- Initial pH;
- Reactant absolute concentrations;

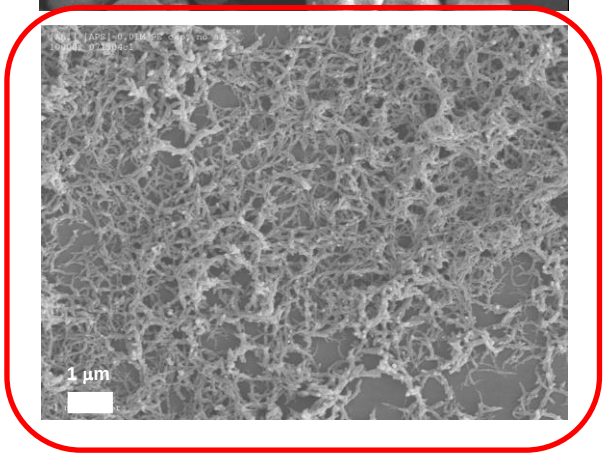


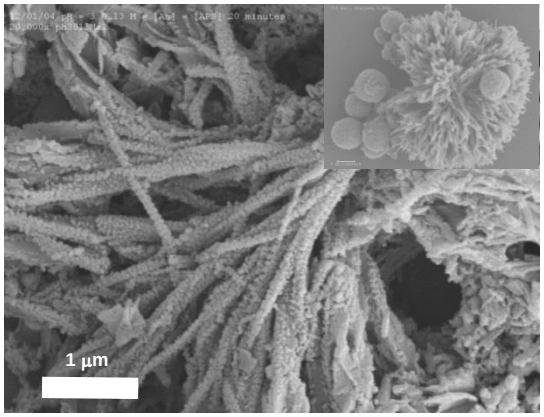








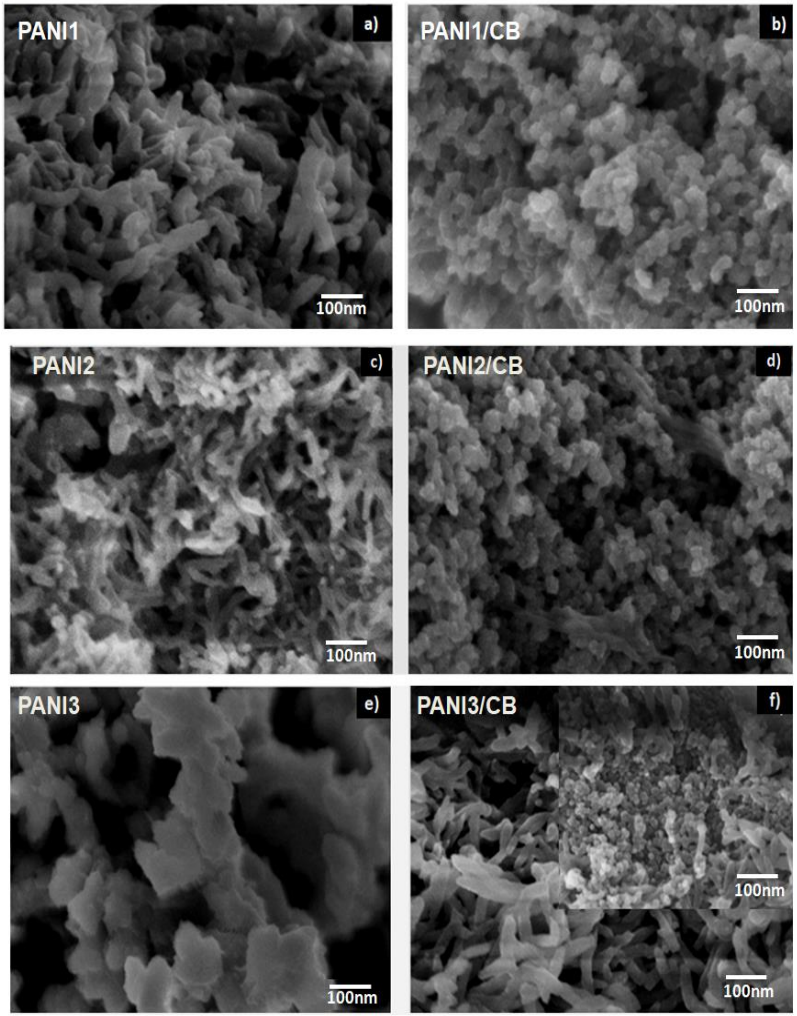


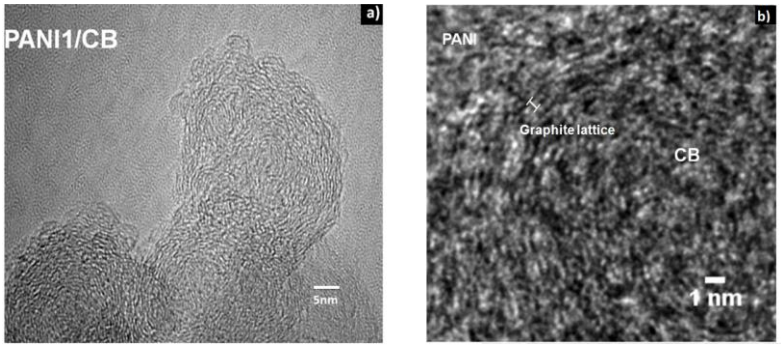


* Venancio,Wang, MacDiarmid. ***Synthetic Metals***, 2006;

Wang, Venancio, Sarno, MacDiarmid. ***Reactive and Functional Polymers***, 2009.

Polyaniline/Carbon Black





TEM bright-field images of core-shell structures of PANI1/CB (a). In (b): Distorted graphite lattice of CB.

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Polyaniline/Carbon black nanocomposites: The role of synthesis conditions on the morphology and properties

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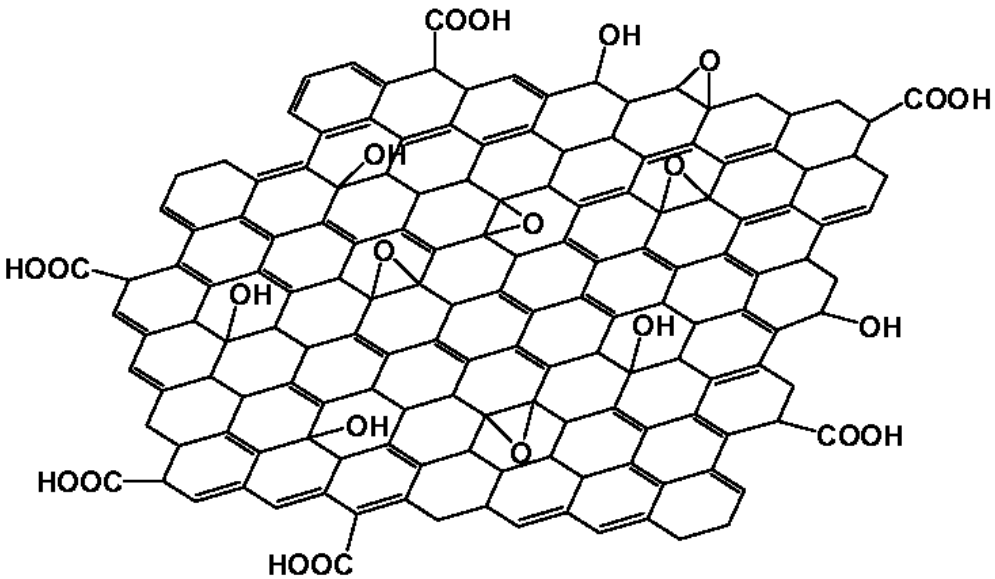
Conducting Polymers Applications

Energy Conversion and Storage devices

Grafene Oxide (GO)/Conducting Polymers

GO Work Function ~ 4,9 eV [1]

- GO [2]
- PEDOT:PSS/GO[2]
- PANI:PSS[3]
- PANI:PSS/GO



GO Band Gap ~ 3,5 eV **hydrophilic**

1. Chhowalla, M. et al. ACS Nano, 2010, 4: 3169–3174 2. Song, M. H. Applied Materials & Interface, 2014. 6: 2067–2073 3. Jo. W. H, Solar Energy Materials & Solar Cells 2014, 130: 599 – 604.

PANI/GO Nanocomposites

Water-dispersibility

- directly deposited as conductive electrodes
- process does not require further heat treatment
- uniform coating
- more environmentally friendly than organic solvents

Polyaniline

- Modified “conventional” chemical synthesis*;
- Room temperatura;
- Dodecylbenzenesulfonic acid (DBSA);
- Ammonium peroxydisulfate;

*Venancio, E.C.; Wang, P.C.; MacDiarmid, A.G. Synthetic Metals
Lemos, H.G.; Santos, S.F.; Venancio, E.C. Synthetic Metals

Experimental - Synthesis of GO

Hummers' Method

H_2SO_4, $NaNO_3$ and $KMNO_4$

High temperature ~ 98ºC

Modified Hummers' Method

H_2SO_4, $NaNO_3$ and $KMNO_4$

Improved Method

H_2SO_4/H_3PO_4 and $KMNO_4$

Without formation of toxic gases

Temperature ~ 35ºC

Tour, J.M. et al. *ACS Nano*, 2010, 4: 4806-4814.

Experimental - Water-Dispersible PANI/GO

PANI/GO and POMA/GO composites

Synthesis "In situ"

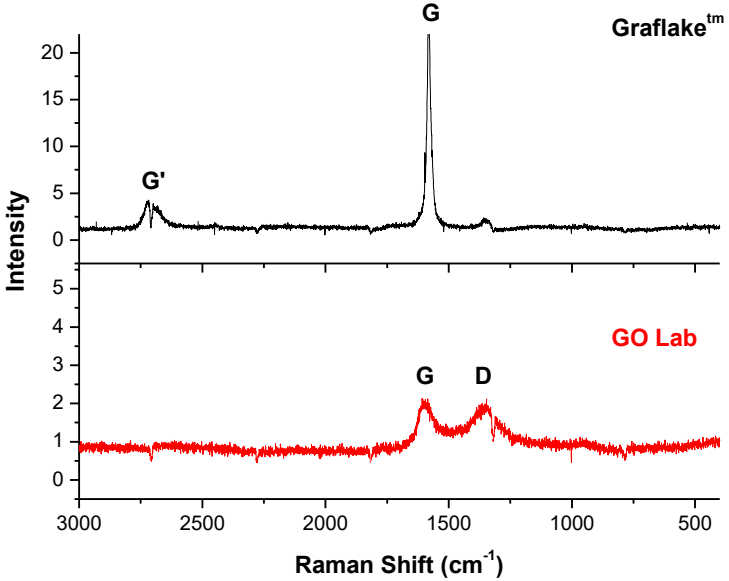
Proportion GO:monomer
0.6 wt%
1.25 wt%
2.5 wt%

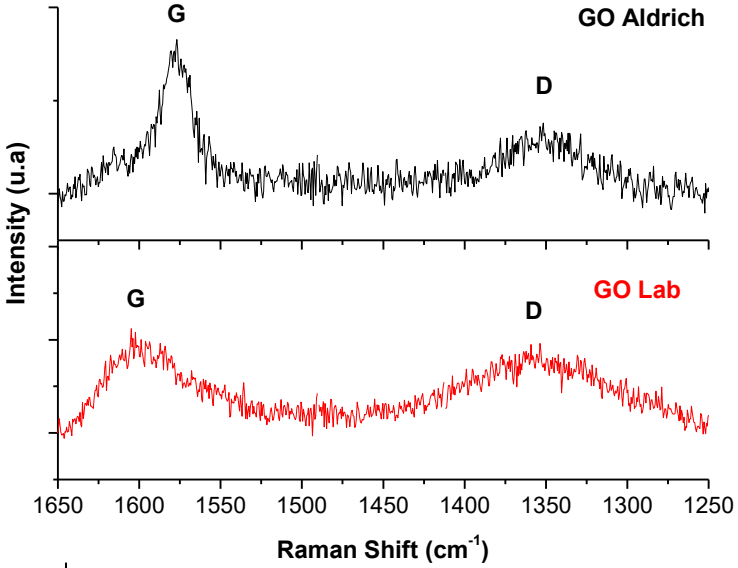
Synthesis "Mixture"

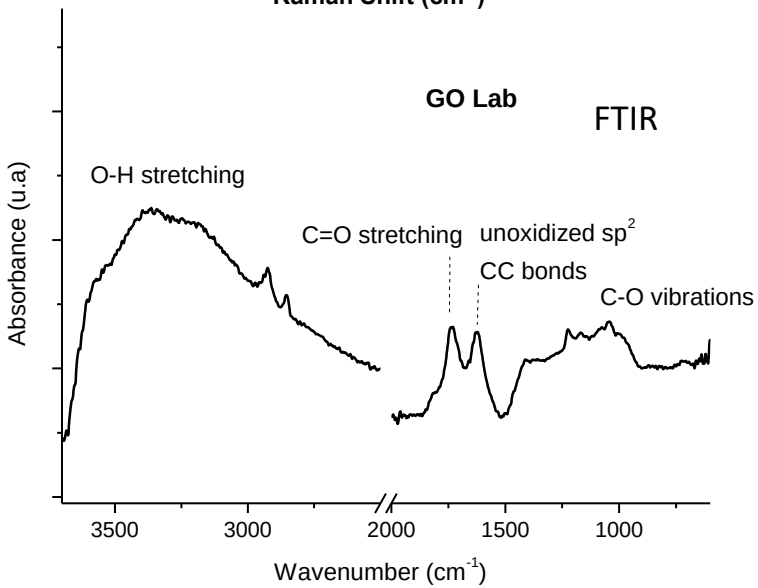
Proportion GO:polymer
0.6 wt%
1.25 wt%
2.5 wt%
5.0 wt%

GO was exfoliated by using sonication

Graphene Oxide Synthesis

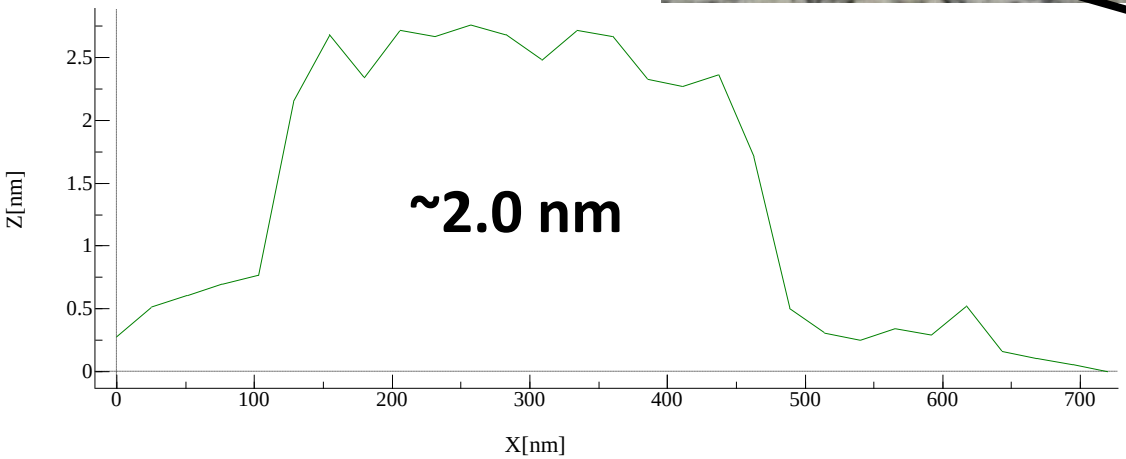


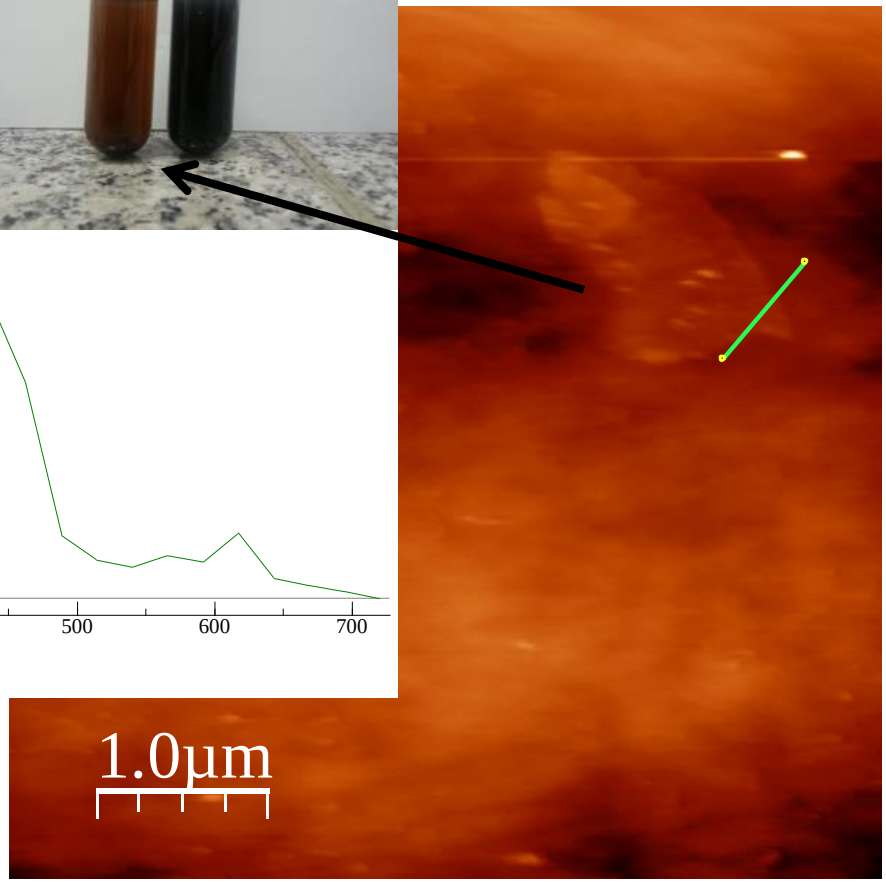




Results – Synthesis of GO

AFM Analysis



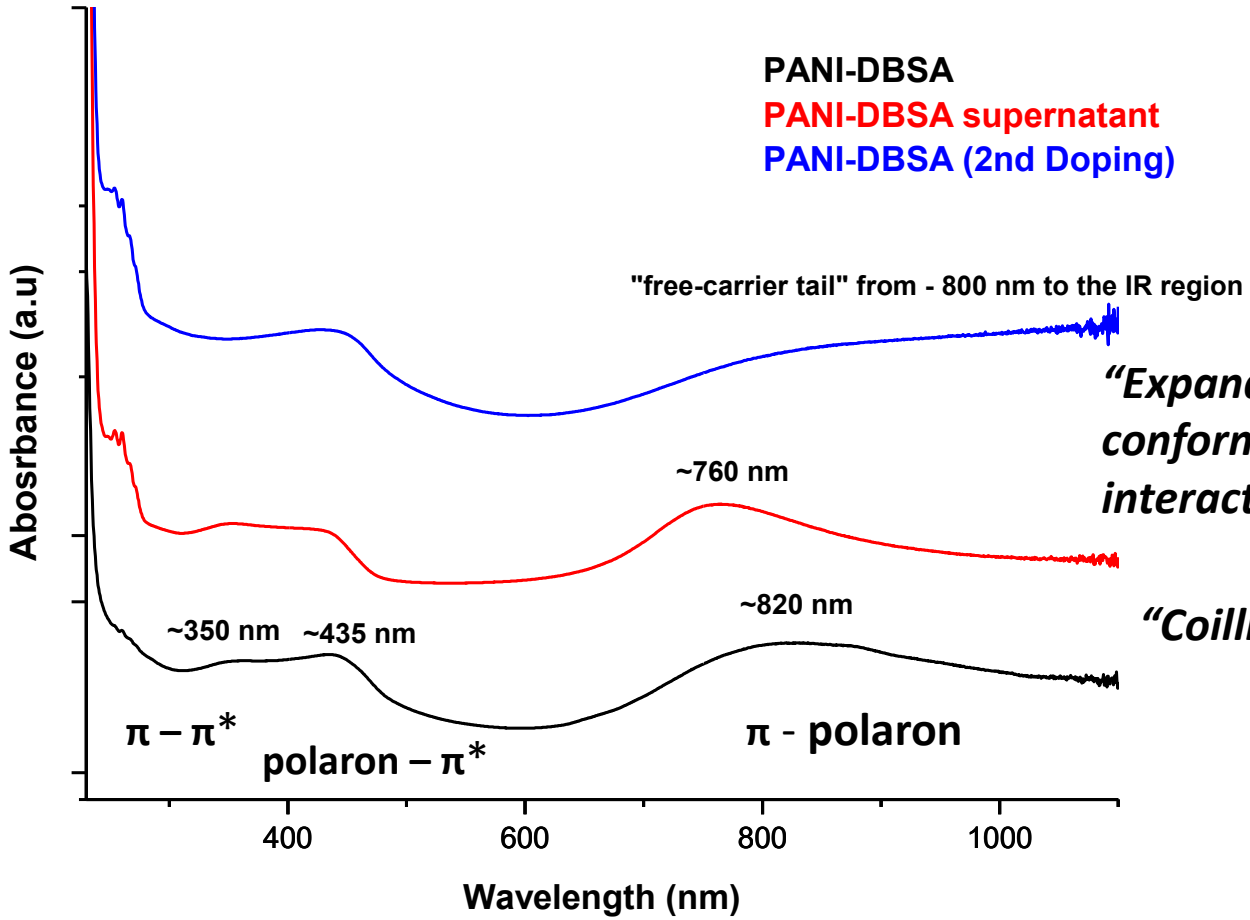


Results

Synthesis PANI-DBSA

Results – Synthesis of PANI-DBSA

UV-Vis Spectroscopy



"Expandaded coil" conformation – greater interaction among the polarons

"Coillike" conformation

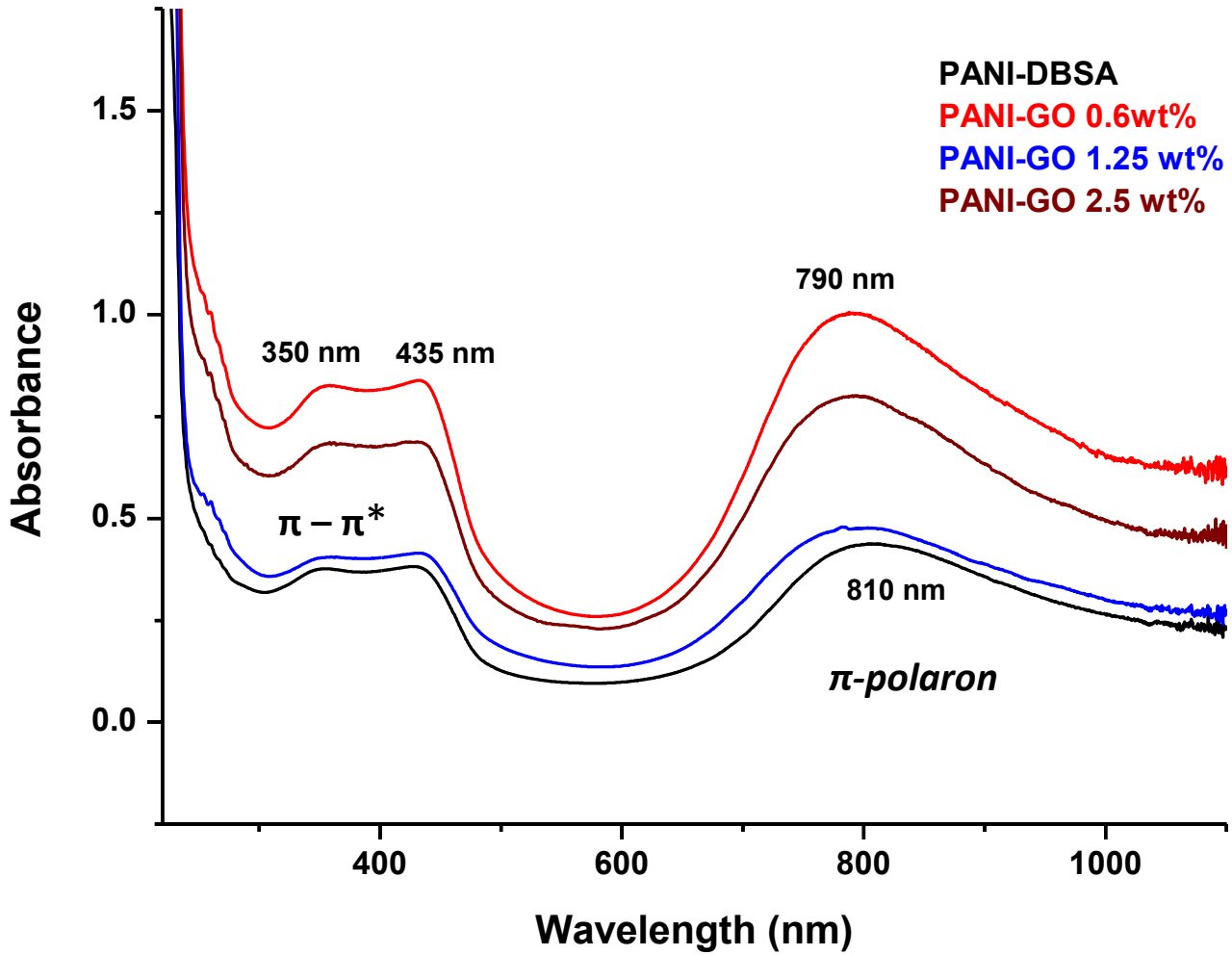
MacDiarmid, A.G. et. al. *Chem. Mat.* 1995; 7: 443 - 445.

Results

Synthesis PANI/GO “In Situ”

Results – Synthesis of PANI/GO "In-situ"

UV-Vis Spectroscopy



Increase of the relative intensity of the π – π to the polaron – π* band when adding GO*

An hypsochromic shift of π-polaron band

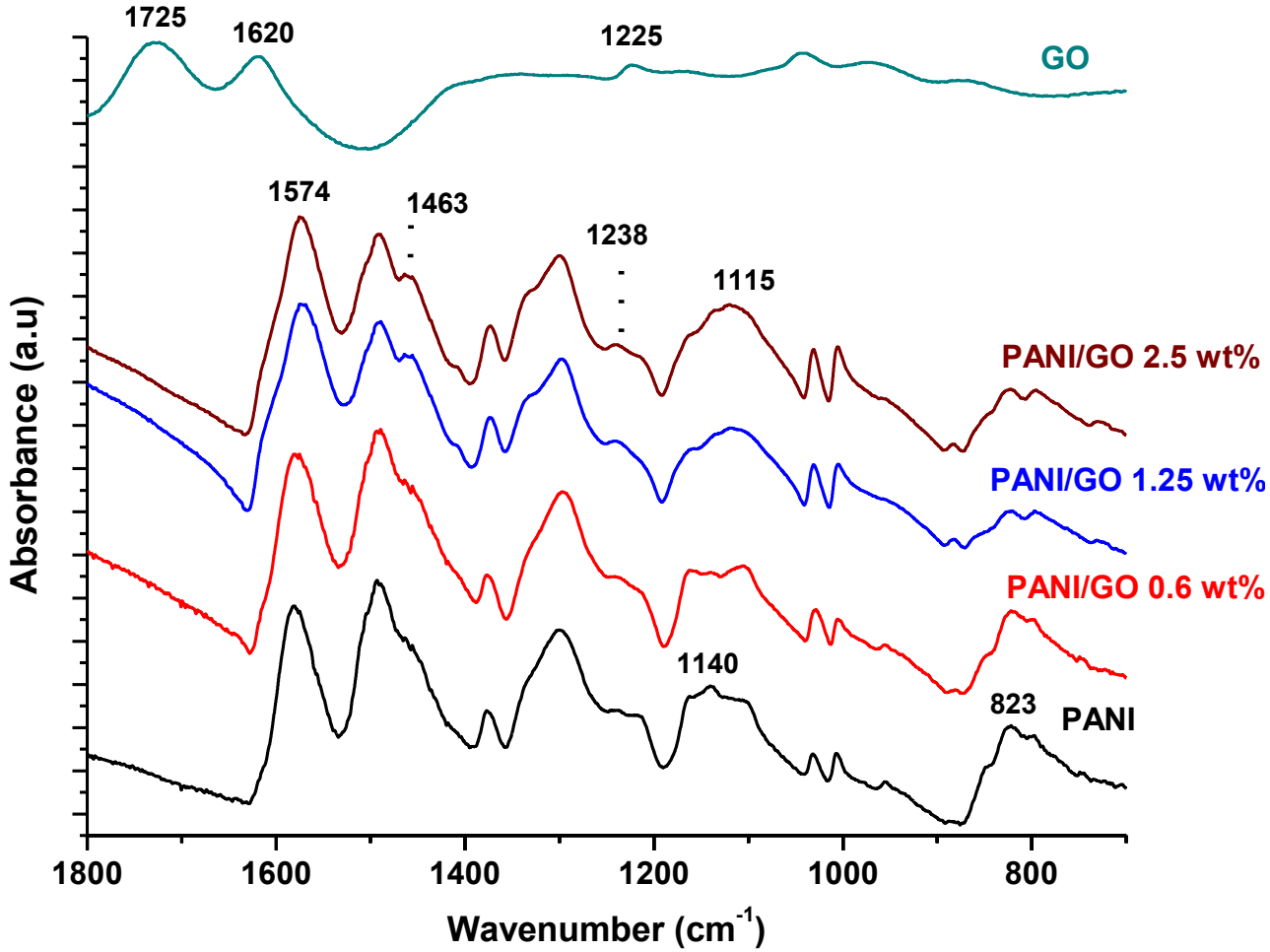
GO – nucleation sites
Different morphlology?

SEM/TEM

XRD

Results – Synthesis of PANI/GO "In-situ"

FTIR analysis



Protonation:

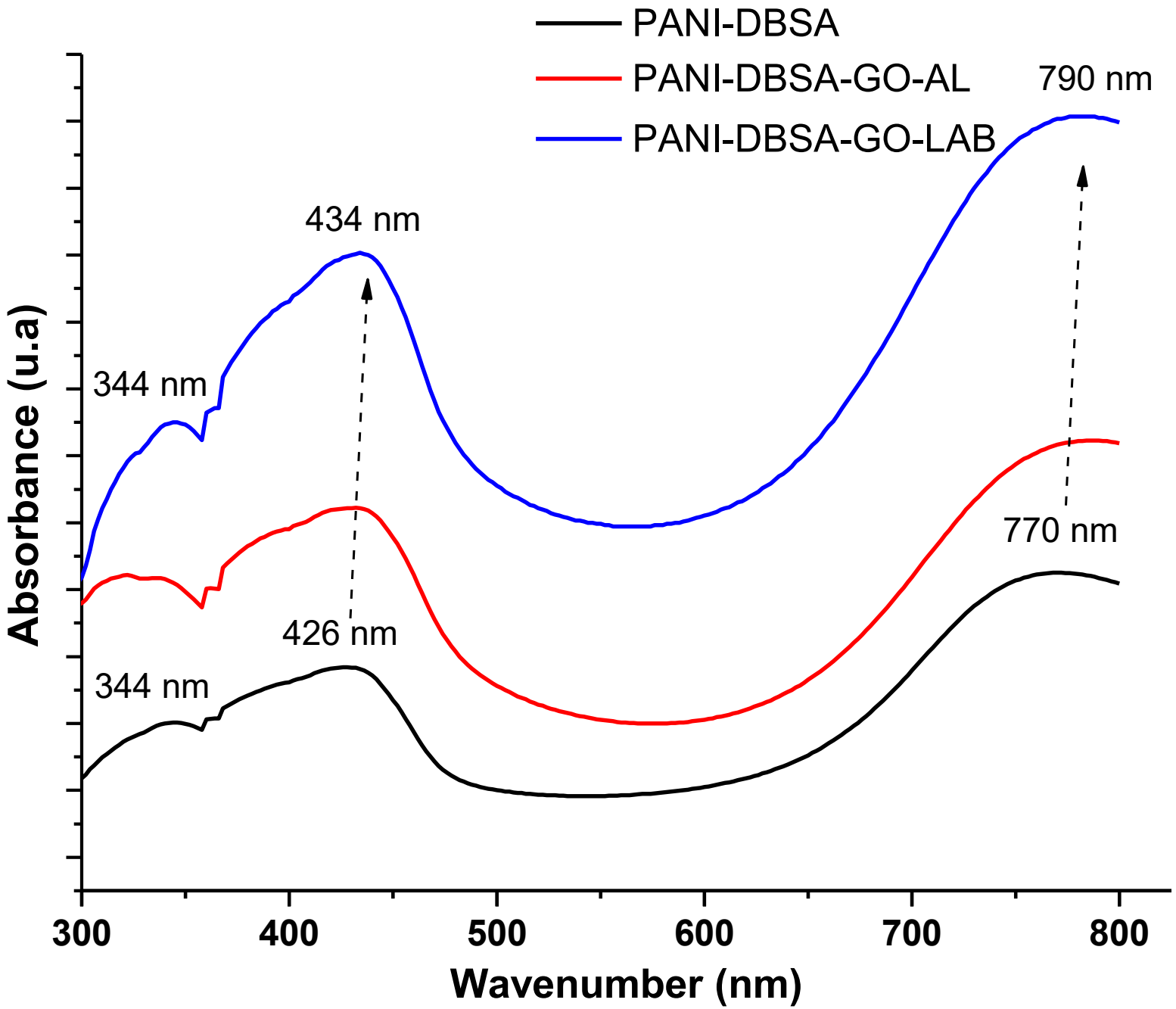
Emerging band at 1463 cm^{-1} – benzoid unit

Shift at 1140 cm^{-1} – C-C deformation plan

Emerging band about 1238 cm^{-1} - consistent with N-H bending and C-N stretching

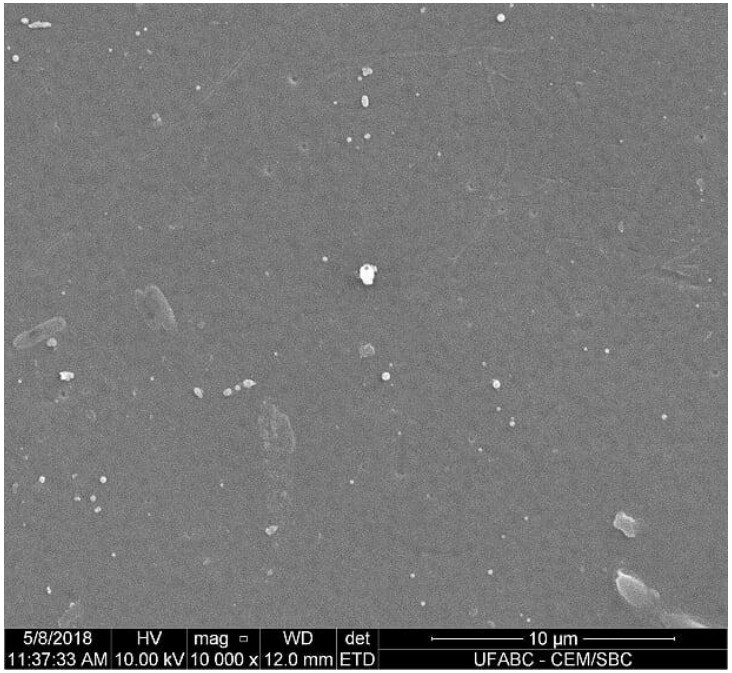
These spectrum suggest that the functional groups from GO are likely linked on the nitrogen of PANI backbone via doping process

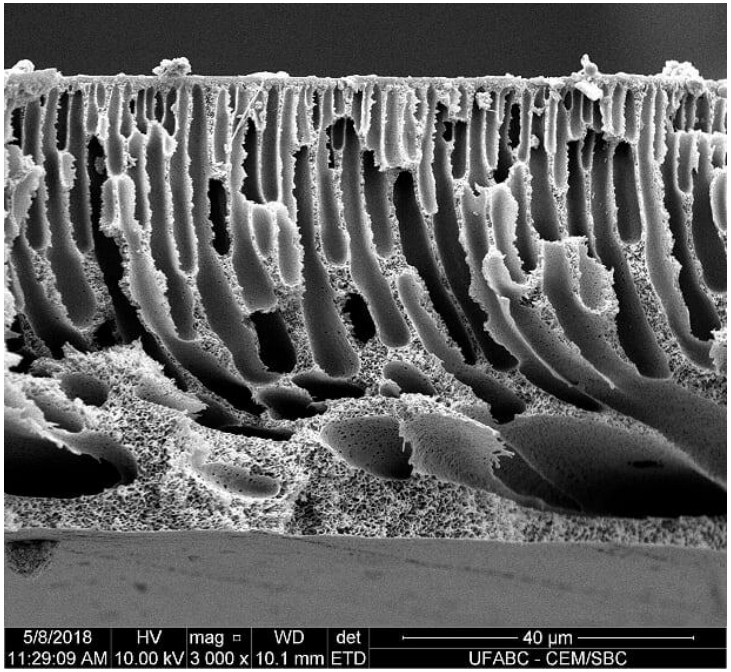
Lemos, H.G., Santos, S.F., Venancio, E.C. *Synthetic Metals* 2015; 203: 23-30.


PANI-DBSA
PANI-DBSA-GO-AL
PANI-DBSA-GO-LAB
790 nm
434 nm
344 nm
770 nm
426 nm
344 nm
Absorbance (u.a)
300
400
500
600
700
800
Wavenumber (nm)

Wastewater Treatment

Poly(ethersulfone)/PANI-rGO





Hugo G. Lemos, Jamile Gonçalves, Eduardo L. Subtil – CECS/UFABC

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- Mathilde J.G. Champeau Ferreira – CECS/UFABC
- Sydney F. Santos – CECS/UFABC
- Eduardo L. Subtil – CECS/UFABC

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