GraphITA
15-18 May 2011
Gran Sasso National Laboratories (Assergi-L'Aquila, Italy)

Simultaneous Reduction of Graphene Oxide and Polyaniline

Doping-Assisted Formation of a Solid-State Charge-Transfer Complex

W.K. Maser
C. Vallés, P. Jiménez, E. Muñoz, A.M. Benito

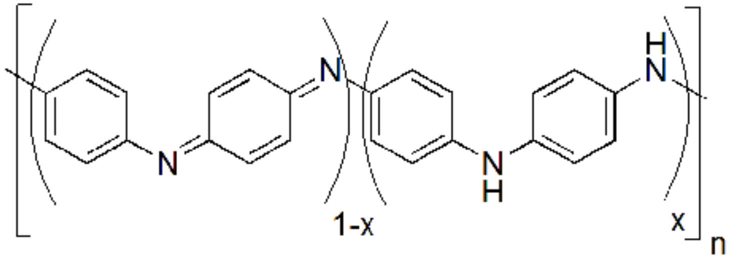
Group of Carbon Nanostructures and Nanotechnology
Instituto de Carboquímica ICB-CSIC
Zaragoza

INSTITUTO DE CARBOQUIMICA

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

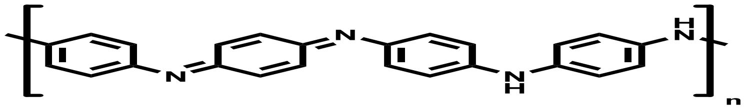
POLYANILINE: STRUCTURE

General Structure of PANI

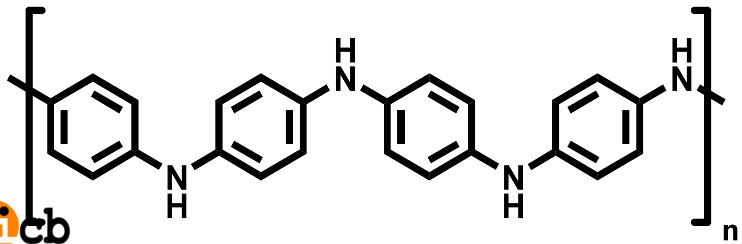


Mixed oxidation state polymer

Pernigraniline



Emeraldine **Base (EB)**



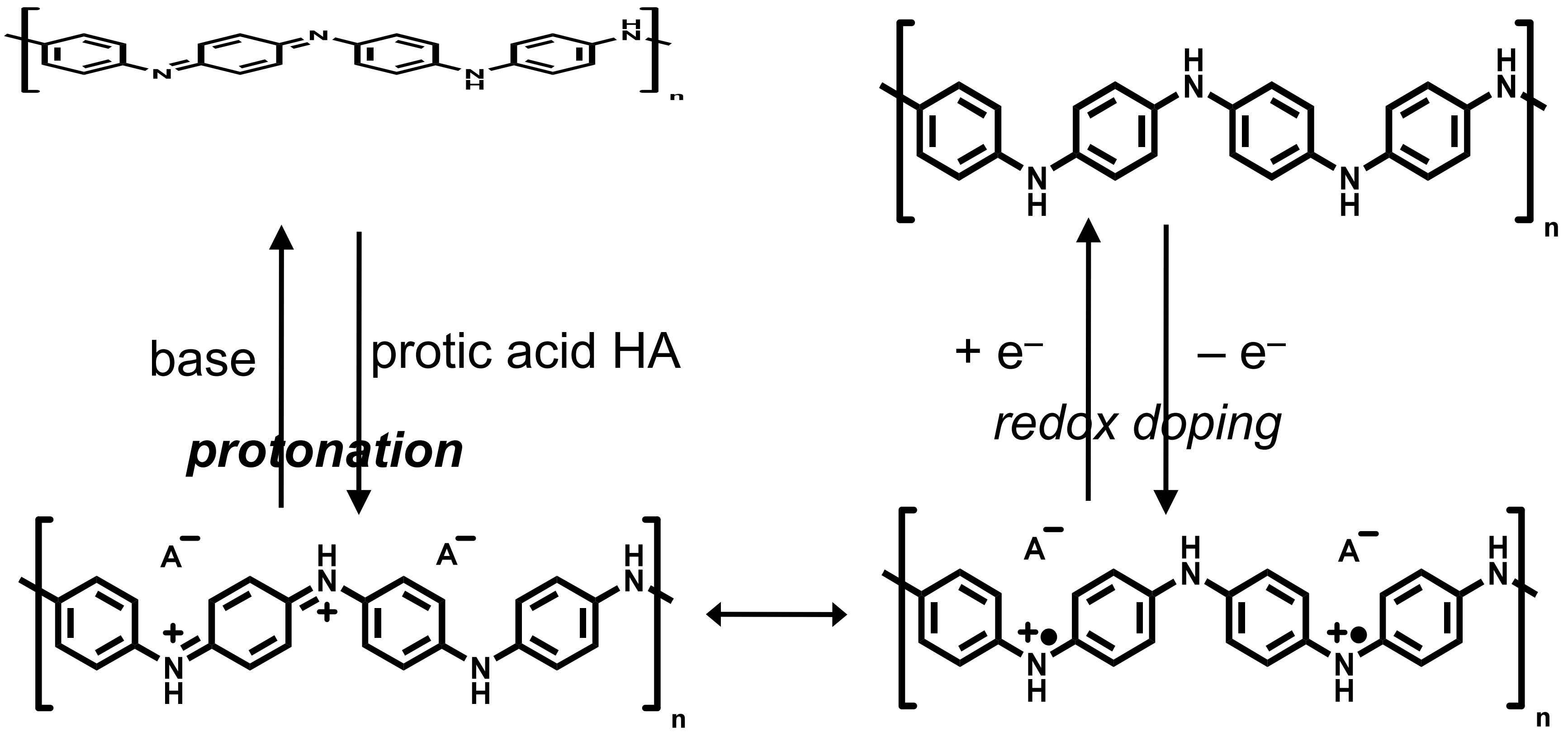
LeucoEmeraldine **(LE)**

DOPING CHEMISTRY

Emeraldine **base (EB)**

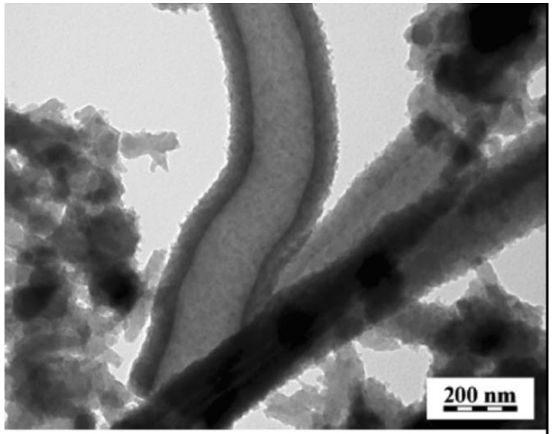
Leucoemeraldine **(LE)**

Non-conducting



Emeraldine **salt (ES)**

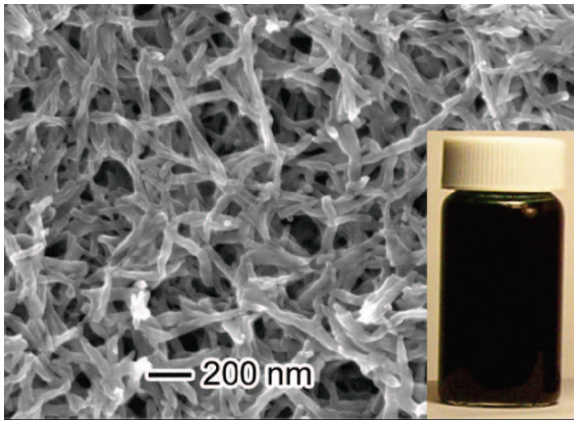
doped state ((highly) conducting)



1D: PANI **nanofibers**

Intrinsic morphology of PANI: easy and direct synthesis
D. Li, R.B. Kaner, JACS, 2006, 128, 968

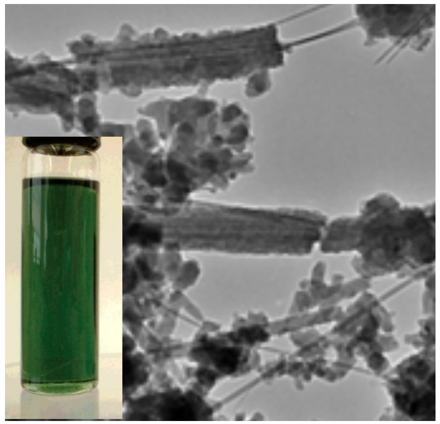
nf-PANI



High specific surface area
High dispersibility

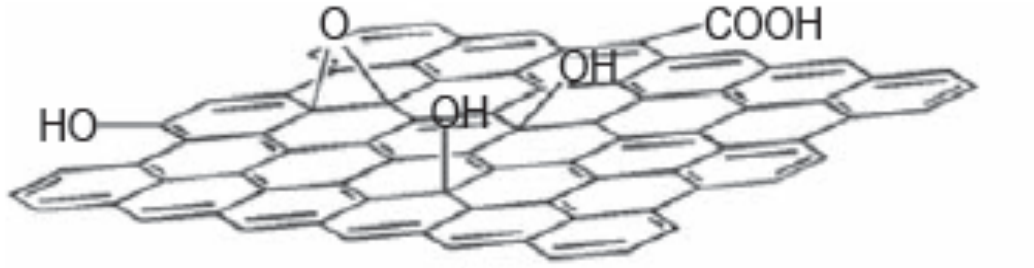
Nf-PANI/MWNT (50 wt%)
In water (10mg/mL)

nf-PANI/MWNT

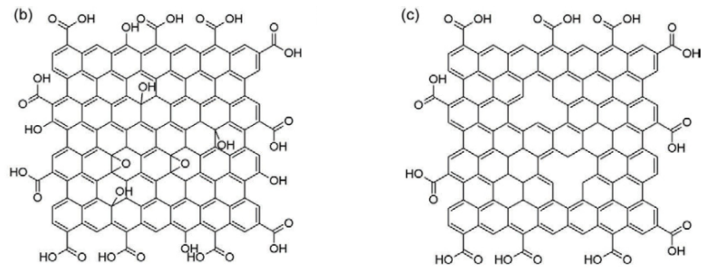


P. Jiménez, Marcomol. Rapid. Commun. 2009, 30, 418
Patent: PCT/ES2009/070021

Graphene Oxide



- Ease of synthesis (large scale)
- Water solubility
- Control of conductivity (reduction)
- Large surface area



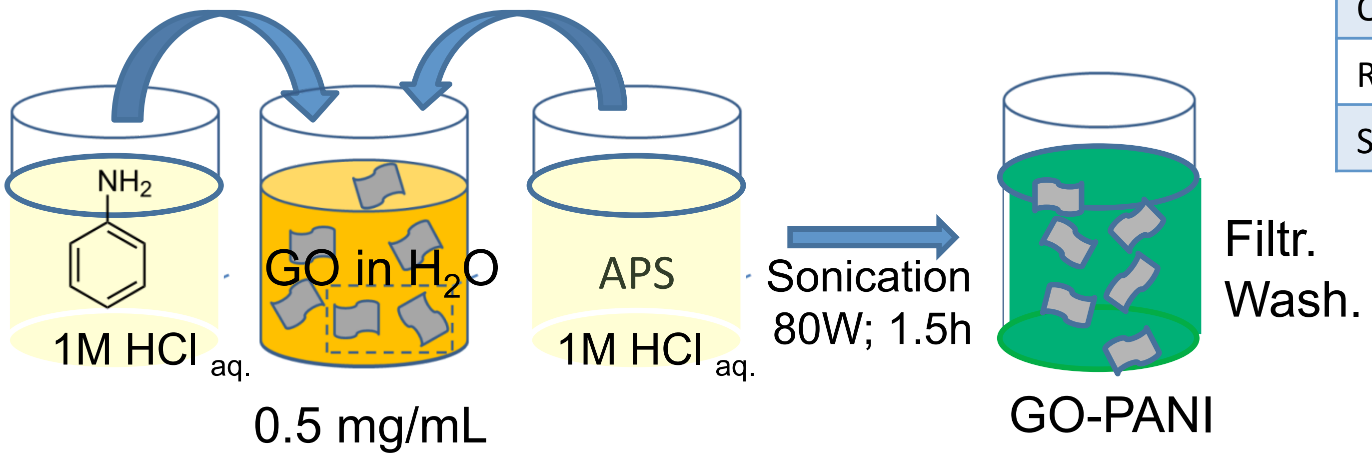
Graphene Oxide & nf-PANI

- Many similarities
- Highly compatible

SYNERGETIC EFFECTS

GO-PANI & R(GO-PANI)

Step 1: *In-situ* polimerization



GO : aniline= 1 :1

Temperature	15-18 ºC
Acidity pH	≈ 1.5
Reactant conc.	0.5 mg/mL
Oxidant / Aniline	0.31
Reaction volume	100 mL
Sonication power	80 W

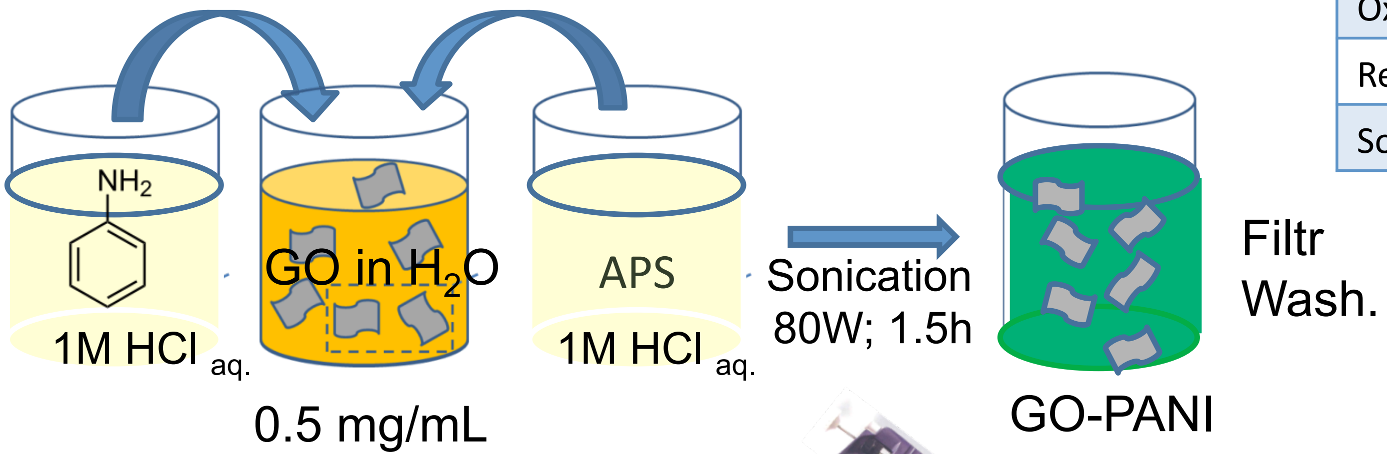
nf-PANI conditions

SYNTHESIS GO-PANI

GO-PANI & R(GO-PANI)

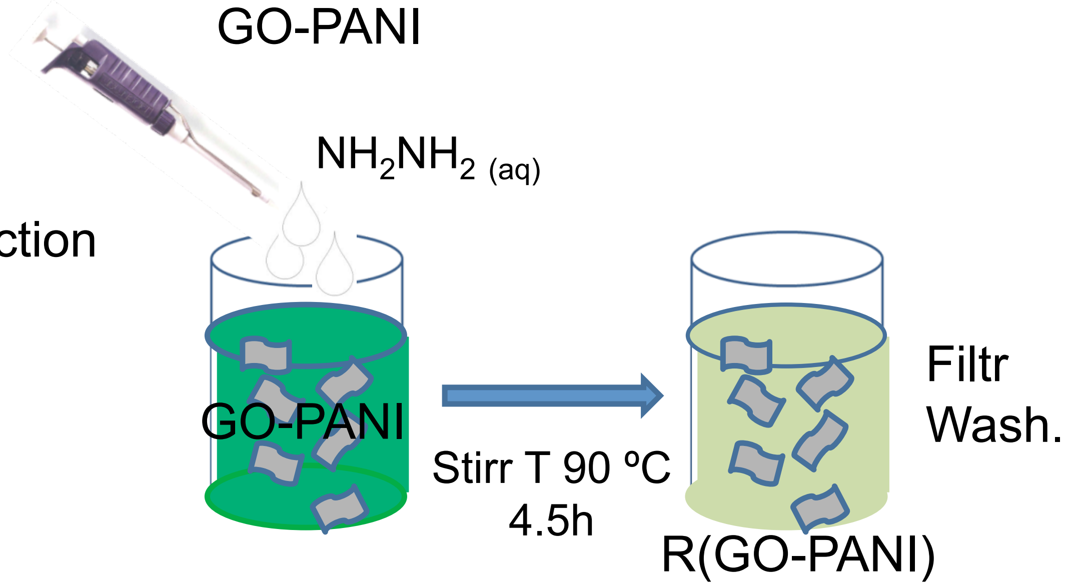
Temperature	15-18 ºC
Acidity pH	≈ 1.5
Reactant conc.	0.5 mg/mL
Oxidant / Aniline	0.31
Reaction volume	100 mL
Sonication power	80 W

Step 1: *In-situ* polimerization



GO : aniline= 1 :1

Step 2: Reduction



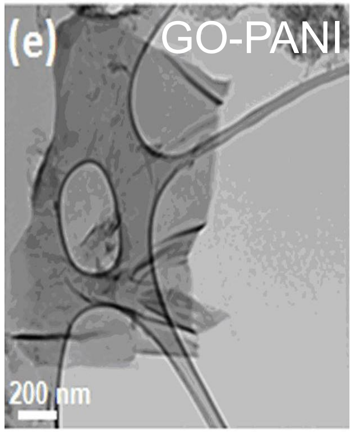
Hydrazine hydrate : GO_{susp}	6µL/mL
Temperature	90 ºC stirr
Time	4.5 h

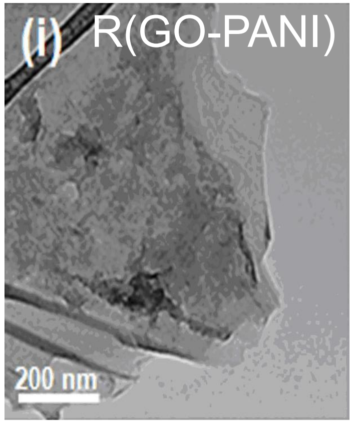
INSTITUTO DE CARBOQUIMICA

CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

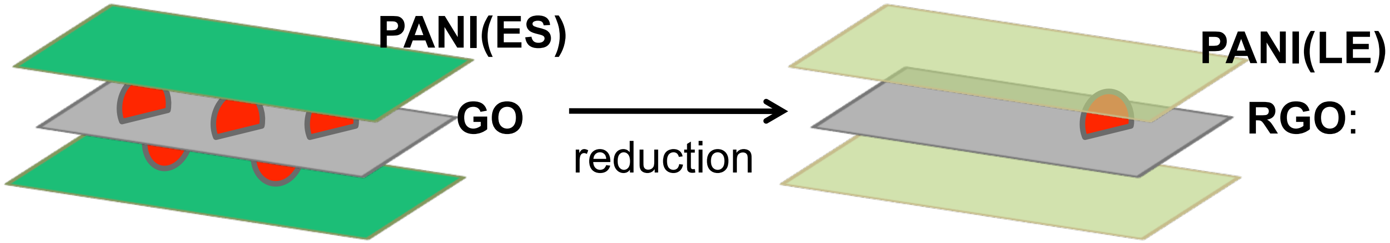
MORPHOLOGY

TEM





Elemental Analysis	Calculated wt% PANI/Graphene
GO-PANI	0.85
R(GO-PANI)	1.01



GO sheets: **TEMPLATE** for aniline nucleation and polymerization
GO-PANI: **THIN LAY ER COATING** of GO by PANI (for 1:1 GO/aniline)
R(GO-PANI): **THIN LAYER COATING RGO by PANI** maintained

MORPHOLOGY = f(SYNTHESIS CONDITIONS)

PROPERTIES COMPOSITE

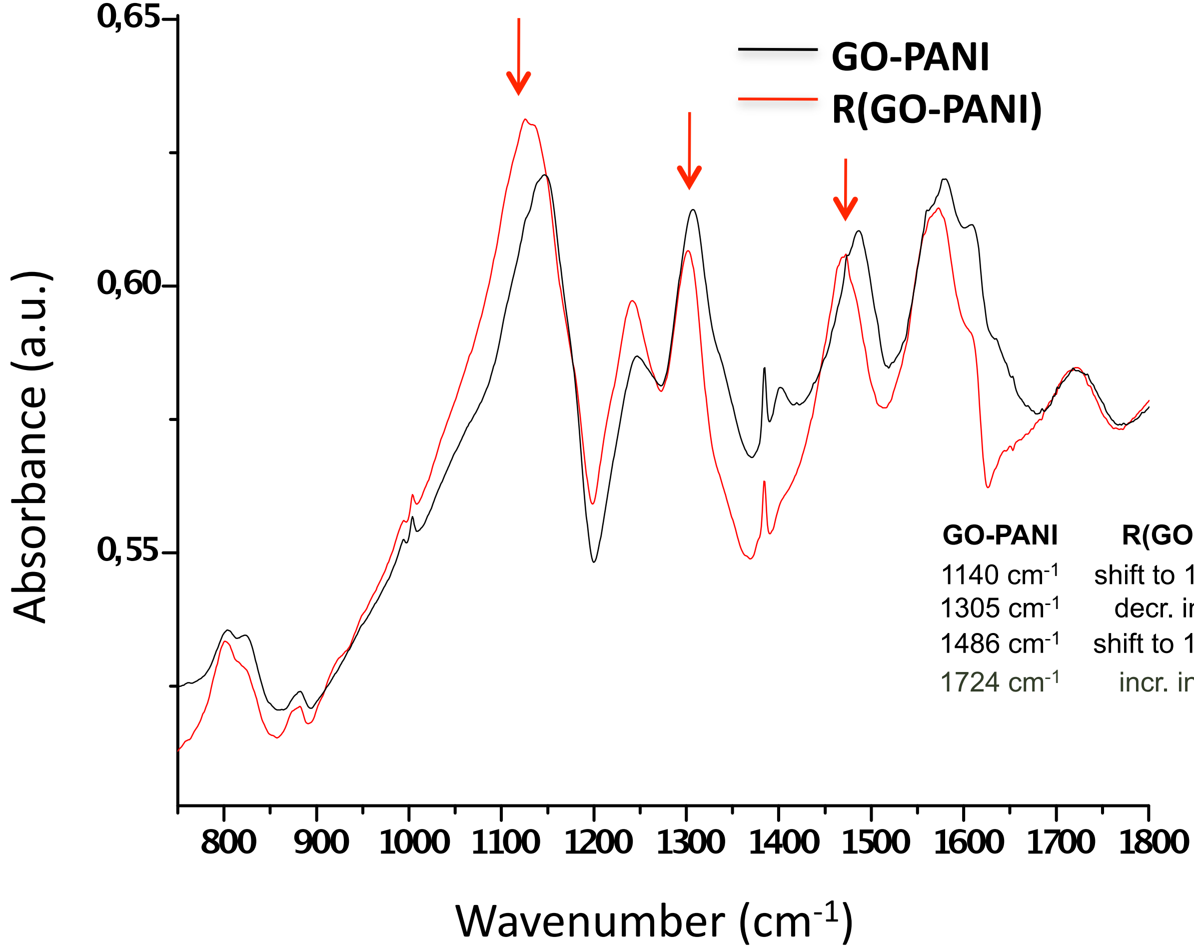
	GO/PANI	R(GO/PANI)
♦ Conductivity	300 S / m	2600 S / m
♦ Thermal stability: (TGA)	520 ºC	570 ºC
♦ Morphology:	Laminar (thin coating)	Laminar (thin coating)
♦ Dispersability: (in water)	Good	Good

•Stable, homogeneous
•Easily (re-)dispersible

INSTITUTO DE CARBOQUIMICA

CSIC
Consejo Superior de Investigaciones Científicas

SPECTROSCOPY: IR



GO-PANI	R(GO-PANI)	Assignment
1140 cm^{-1}	shift to 1130 cm^{-1}	=(NH+)-vibration
1305 cm^{-1}	decr. intensity	C-N str.
1486 cm^{-1}	shift to 1470 cm^{-1}	C=C, quinoid rings
1724 cm^{-1}	incr. intensity	carbonyl

GO-PANI: Superposition GO and PANI (ES)

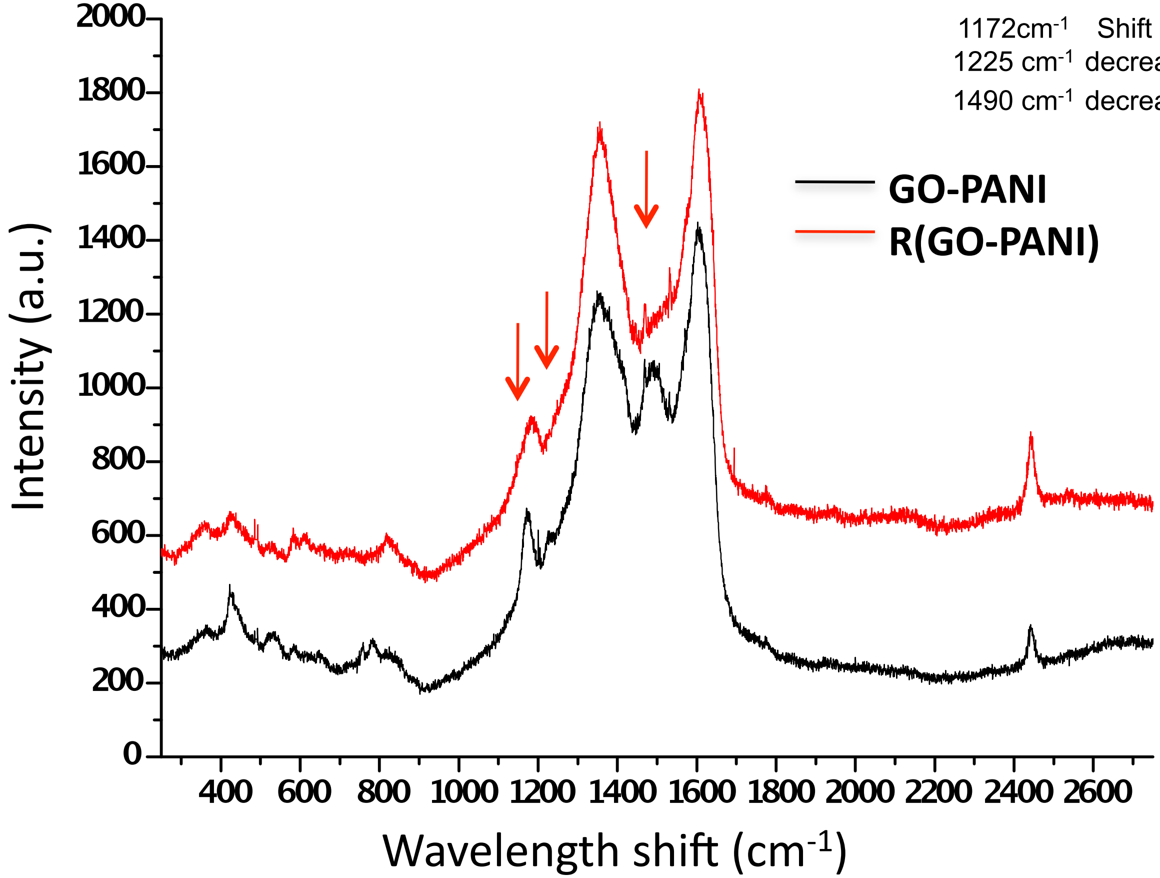
R(GO/PANI): PANI in a partially reduced oxidation state between ES and LE

STABLE! No change of features with time

INSTITUTO DE CARBOQUIMICA

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

SPECTROSCOPY: RAMAN



GO-PANI	R(GO-PANI)	Assignment
1172cm^{-1}	Shift to 1185 cm^{-1}	C-H in plane bend.
1225 cm^{-1}	decreased intensity	C-N str.
1490 cm^{-1}	decreased intensity	C=N, C=C str.

GO-PANI: Superposition of GO and PANI (ES)

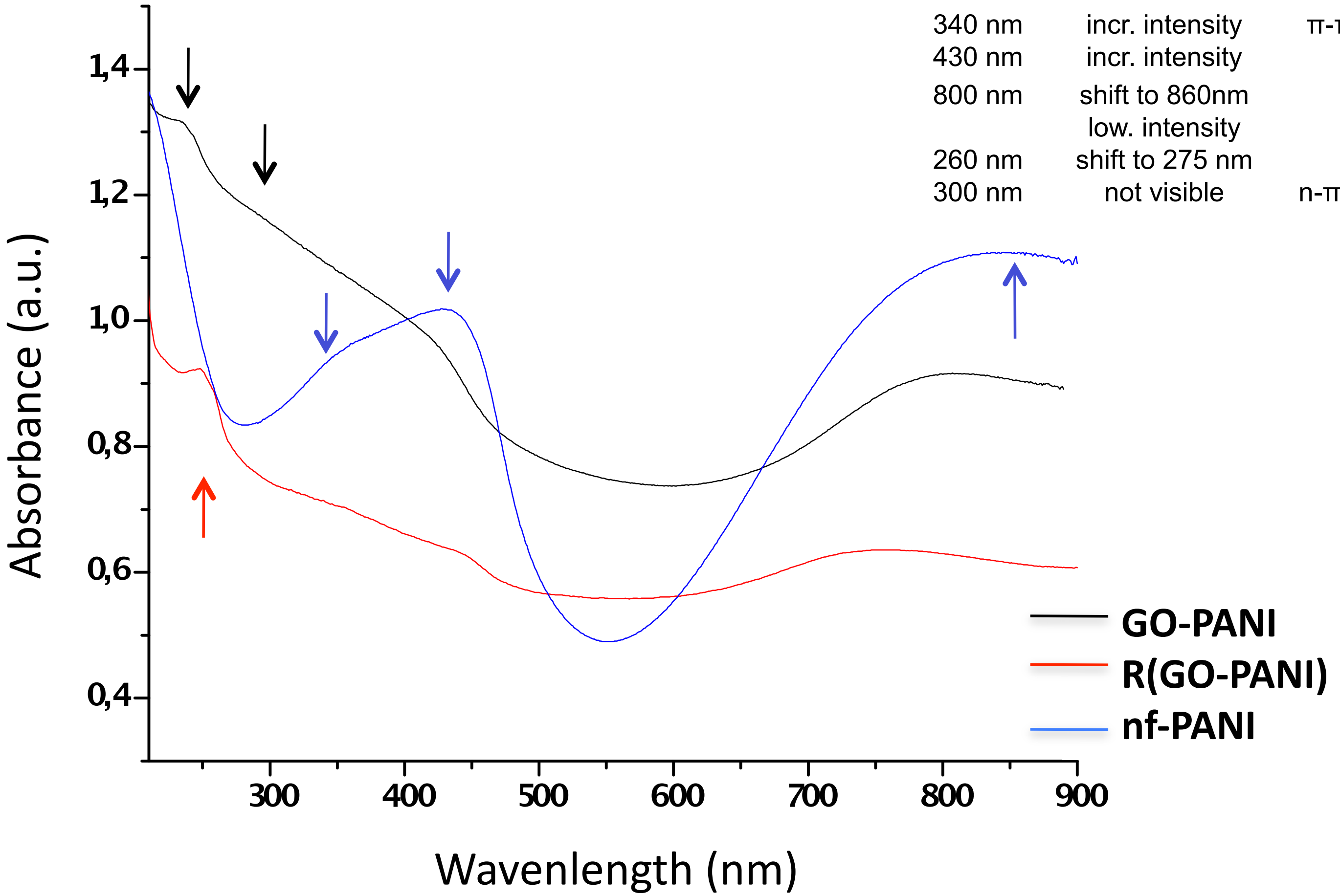
R(GO/PANI): PANI in a partially reduced oxidation state between ES and LE

STABLE! No change of features with time

INSTITUTO DE CARBOQUIMICA

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

SPECTROSCOPY: UV-VIS



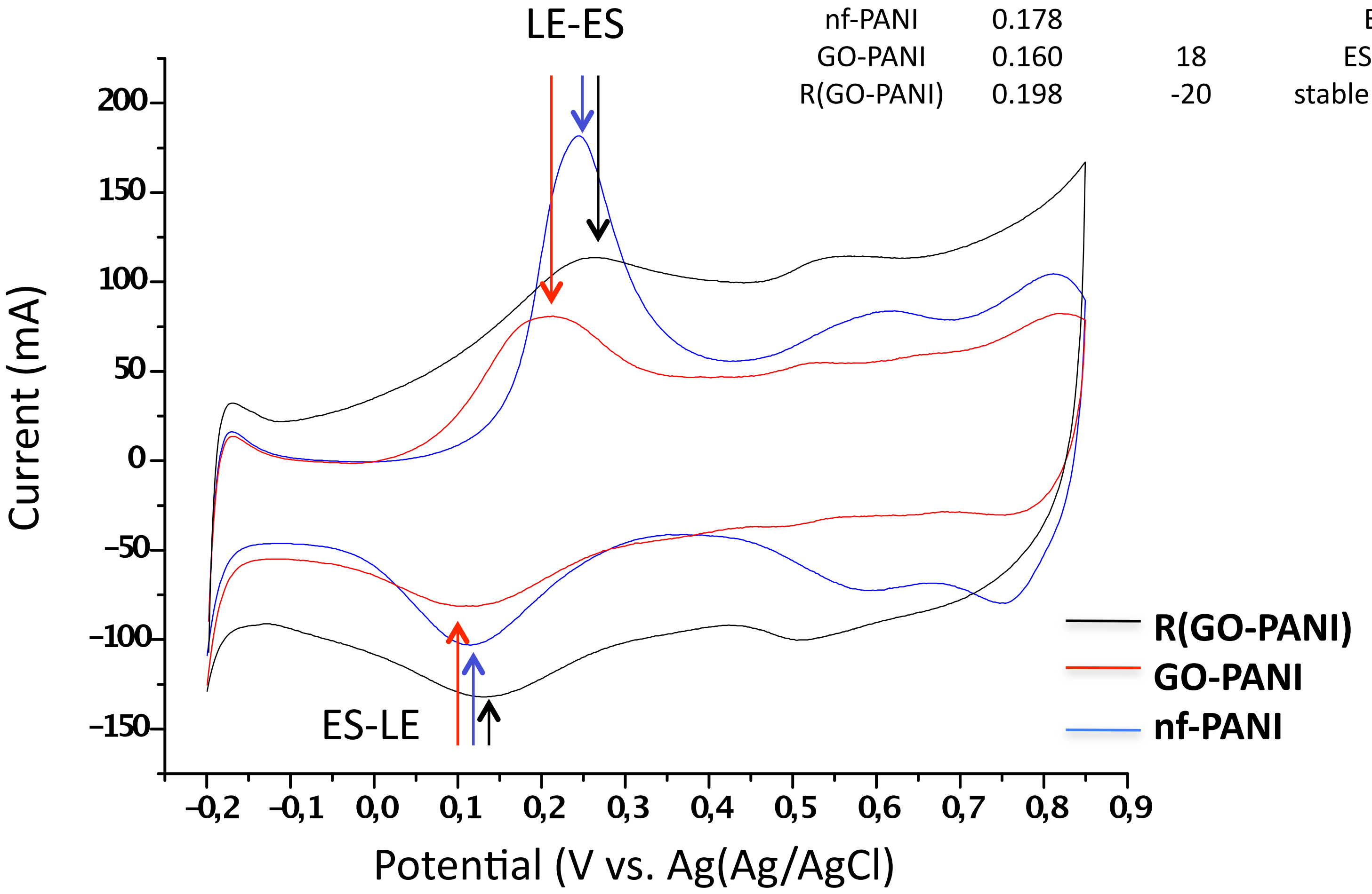
GO-PANI	R(GO-PANI)	Assignment
340 nm	incr. intensity	π-π*, benzenoid rings
430 nm	incr. intensity	polaron-π*
800 nm	shift to 860nm low. intensity	π-polaron
260 nm	shift to 275 nm	π-π* graphene
300 nm	not visible	n-π*, carbonyl moieties

GO-PANI: ES slightly deprotonated: due to carboxylate groups at GO
R(GO/PANI): PANI in a partially reduced oxidation state between ES and LE

STABLE! ALSO IN LIQUID PHASE!

CYCLOVOLTAMMETRY

Trans. LE-ES	$E_{1/2}^{rev}$ (V)	$\Delta E_{1/2}^{rev}$ (mV)	ES state
nf-PANI	0.178		ES
GO-PANI	0.160	18	ES-EB
R(GO-PANI)	0.198	-20	stable (ES-LE)



Intermediate oxidation state does not reoxidize into the ES state.
Stabilitzation of an anomalous oxidation state of PANI in between ES and LE

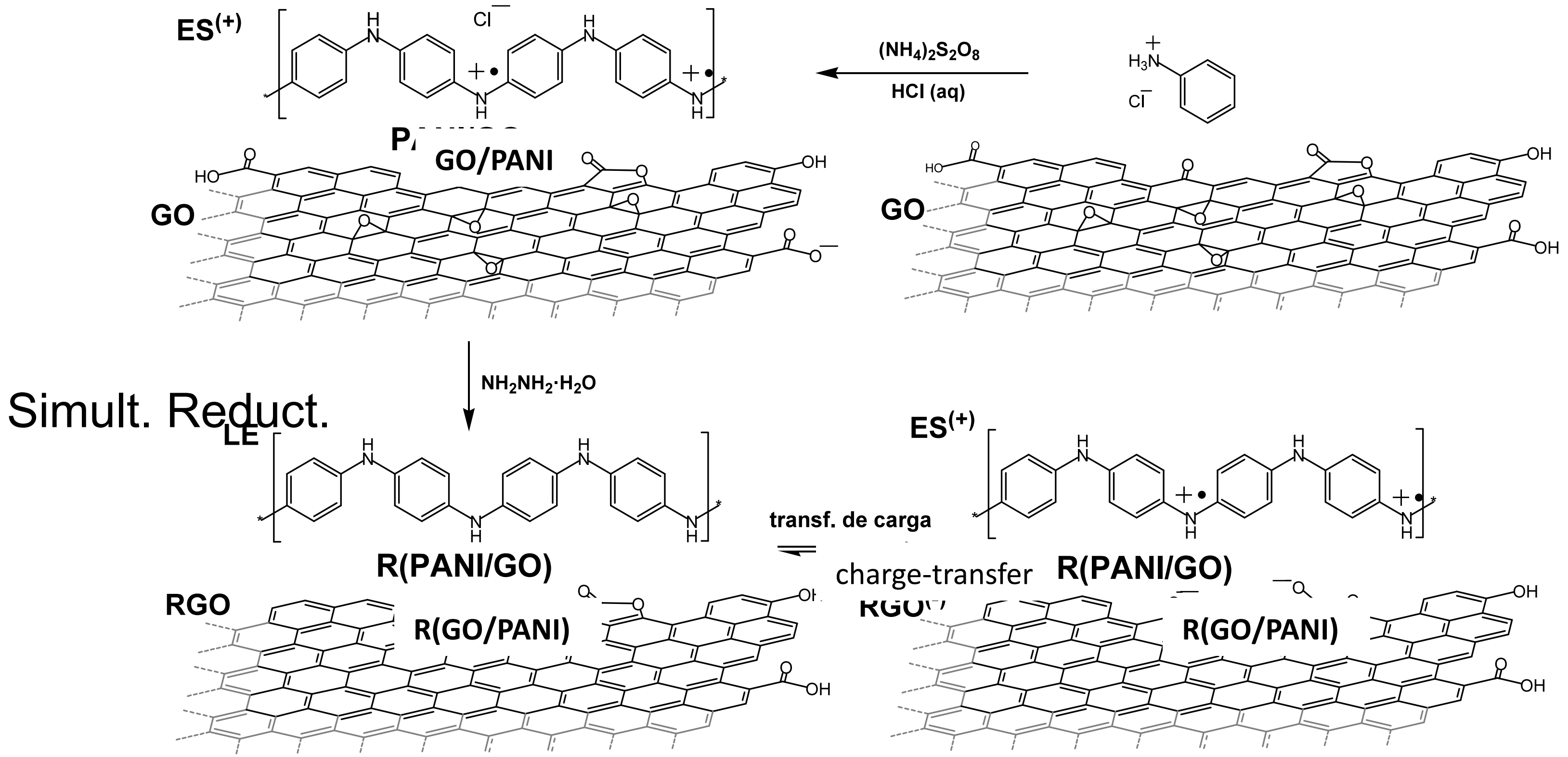
R(GO-PANI)

- Thin PANI layer coating RGO
  → favors interactions at extended RGO-PANI interface
- Stable intermediate oxidation state in between ES and LE
  →Charge-transfer processes are involved
- High environmental degradation stability, in solid and liquid state
- Improved conductivity
- Dispersibility in aqueous media
  → Involvement of charges

Graphene (GO, RGO): excellent electron acceptor

MECHANISM

Formation of a Charge-Transfer Complex



Formation of a donor (LE) - aceptor (RGO) solid-state charge-transfer complex

Double role of RGO: electron acceptor & large counterion of ES

$RGO^{\delta-}$ - PANI $(ES\text{-}LE)^{\delta+}$

INSTITUTO DE CARBOQUIMICA

CSIC Consejo Superior de Investigaciones Científicas

CONCLUSIONS

In-situ polymerization of PANI and GO + simultaneous reduction

- Easy, one pot synthesis route (under ambient conditions)
- Thin PANI coating on GO or RGO
- Stabilization of intermediate PANI oxidation state (ES-LE). Solid & Liquid state

Formation of a Solid-state Charge-Transfer Complex R(GO-PANI)

- Donor-Acceptor interactions at interface RGO-PANI (ES-LE)
- RGO dual role: i) electron acceptor of PANI (LE)
  ii) large anionic counterion of doped PANI (ES)
- Equilibrium partially charged system RGO$^{\delta-}$ - PANI (ES-LE)$^{\delta+}$

ENHANCED MATERIALS PROPERTIES R(GO-PANI)

- Conductivity: 2600 S/m (due to RGO)
- Environmental (chemical and thermal degradation) stability
- High hydrophilicity for both, GO-PANI and R(GO-PANI)
- Excellent water dispersibility for both, GO-PANI and R(GO-PANI)

icb INSTITUTO DE CARBOQUIMICA

CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

OUTLOOK

FUNCTIONAL AND PROCSSABLE (GO – PANI) materials

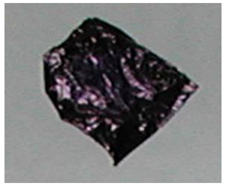
MACROSCOPIC ASSEMBLY
INTO FUNCTIONAL MATERIALS/DEVICES
BASED ON GRAPHENE AND ICPS

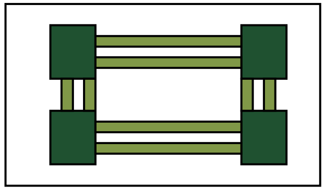
Direct processing

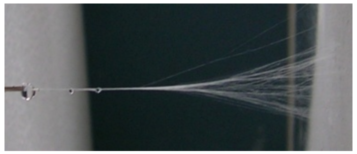
- Coatings
- Casting
- Printing
- Impregnation

Combining with other polymers

•Coatings
•casting
•spinning







•Flexible conducting films and circuits,
•Flexible electrochemical materials/devices

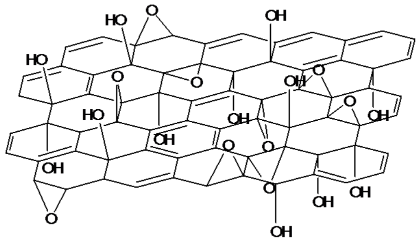
- Conducting fibers
- Membranes,….

FLEXIBLE PLASTIC AND WEARABLE ELECTRONICS

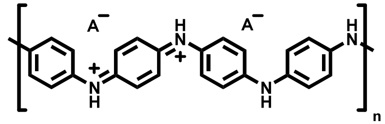
icb INSTITUTO DE CARBOQUIMICA

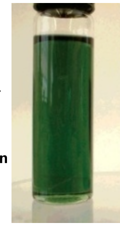
CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

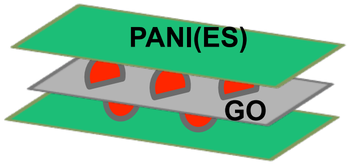
MESSAGE

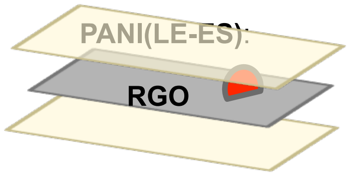


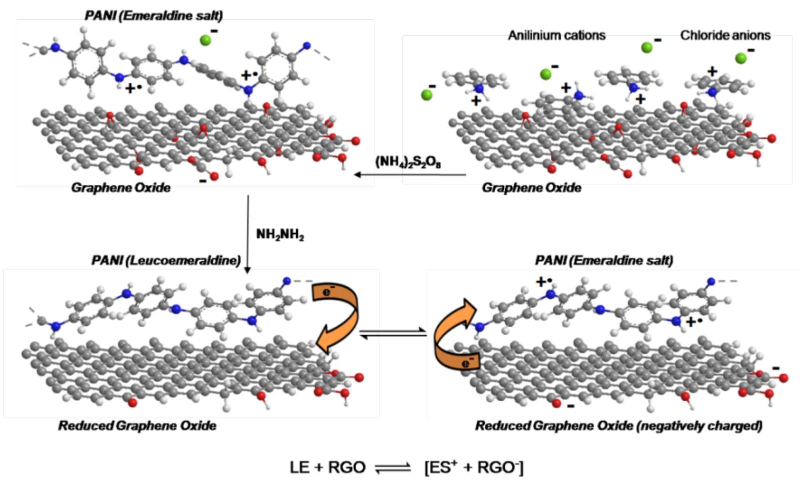
GRAPENE OXIDE & POLYANILIE THE PERFECT FOILS











J. Phys. Chem C online. DOI: 10.1021/jp201791h

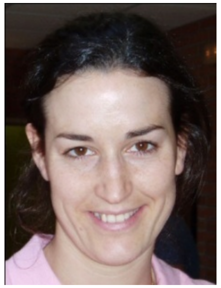
COLLABORATORS

Group of Carbon Nanostructures and Nanotechnology

www.icb.csic.es/index.php?id=g-cnn

Dr. Cristina Vallés

(PG4 RGO papers)



Dr. Pablo Jiménez

Dr. Edgar Muñoz

Dr. Ana M. Benito

International Year of CHEMISTRY 2011

FUNDING

MINISTERIO DE CIENCIA E INNOVACIÓN

MAT2010-15026

UNION EUROPEA
FONDO EUROPEO DE DESARROLLO REGIONAL
"Una manera de hacer Europa"

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

nanotp
NEW - Videos explaining Graphene

FUNDACION RAMON ARECES

GOBIERNO DE ARAGON
Grupo de Excelencia DGA T66

icb
INSTITUTO DE CARBOQUIMICA

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

THANK YOU FOR YOUR KIND ATTENTION