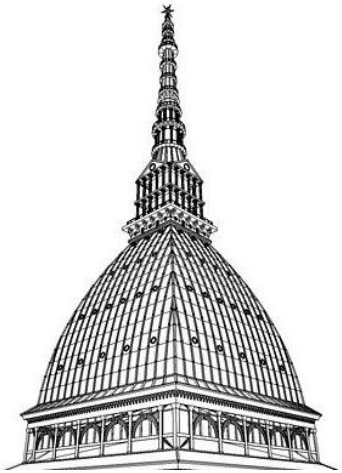
ENABLING TECHNOLOGIES FOR NANOMATERIAL GRAFTING AND COATING



GIANCARLO CRAVOTTO

UNIVERSITY OF TURIN
DEPARTMENT DIRECTOR

Department of Drug Science and Technology
NIS - Centre for Nanostructured Interfaces and Surfaces

PRESIDENT OF THE EUROPEAN SOCIETY OF SONOCHEMISTRY

Università degli Studi di Torino

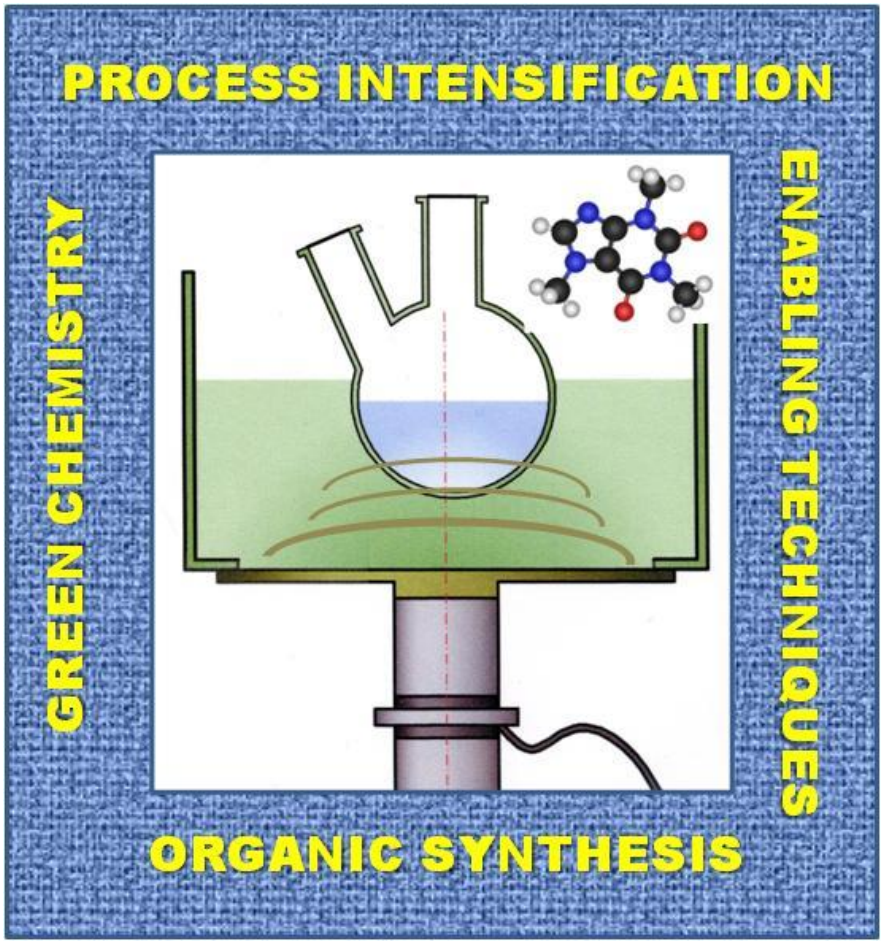
nis CENTRE FOR NANOSTRUCTURED INTERFACES AND SURFACES

DSTF Dipartimento di Scienza e Tecnologia del Farmaco UNIVERSITÀ DI TORINO

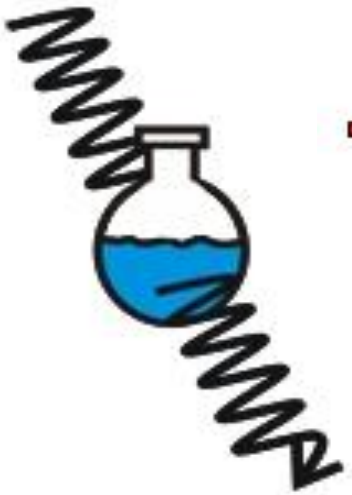
University of Turin founded in 1404 by Prince Ludovico of Savoia under the auspices of Pope Benedict III and the Emperor Sigmund

600
1404-2004
ALMA
UNIVERSITAS TAURINENSIS

A SUSTAINABLE APPROACH TO PROCESS INTENSIFICATION

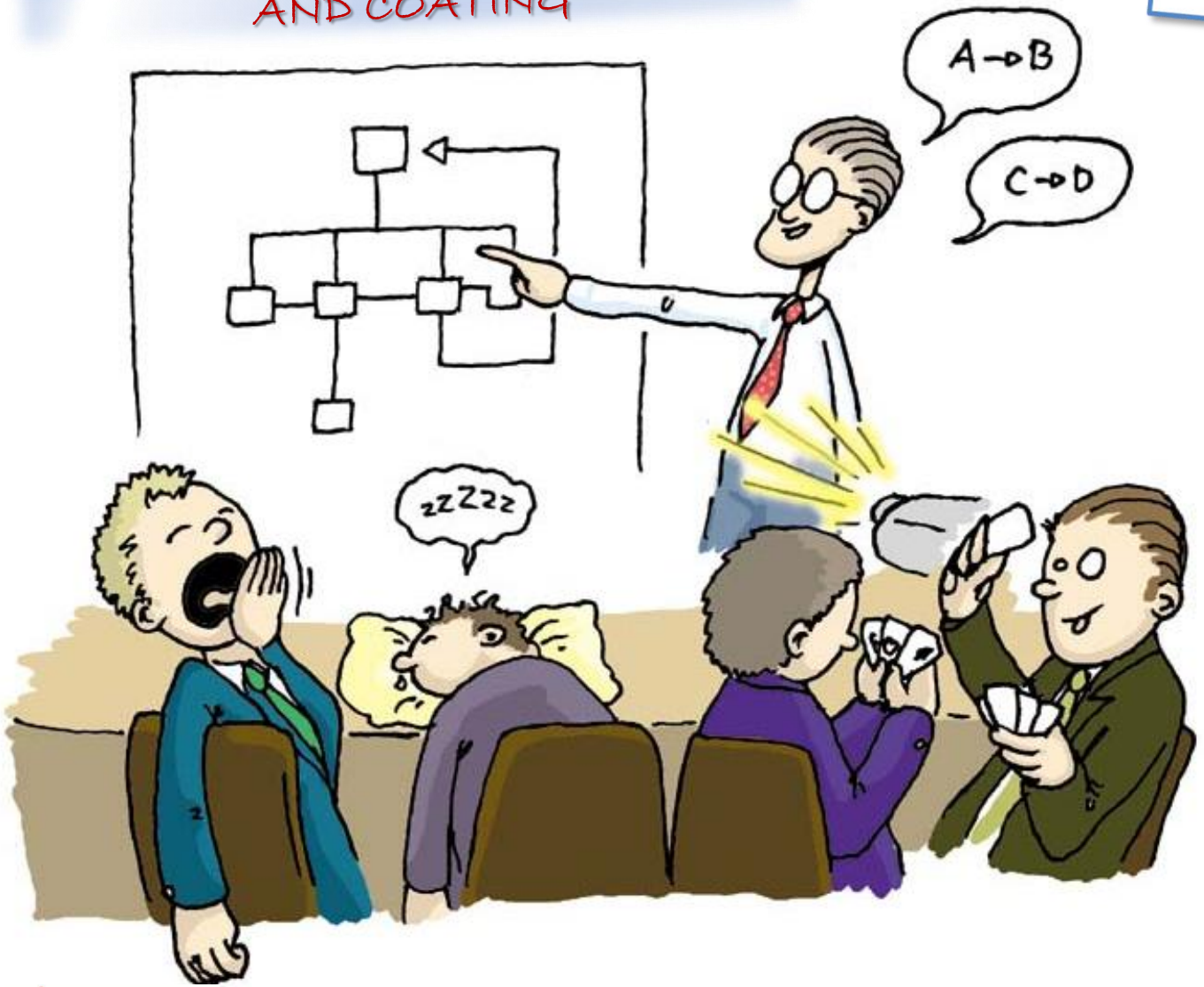


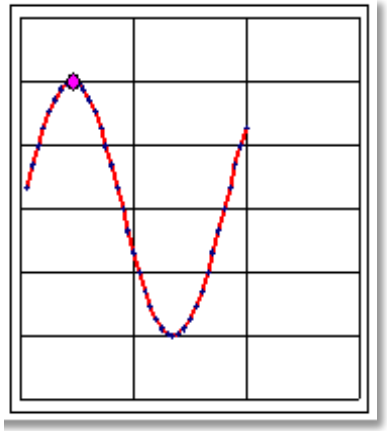
http://www.ocp.unito.it

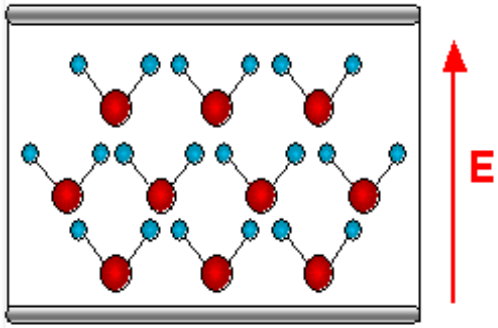


ENABLING TECHNOLOGIES FOR NANOMATERIAL GRAFTING AND COATING

OUTLINE





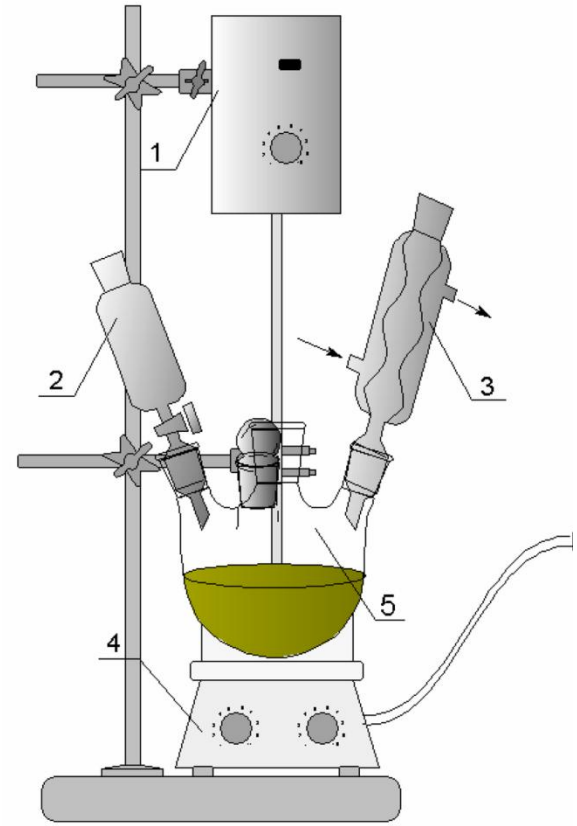


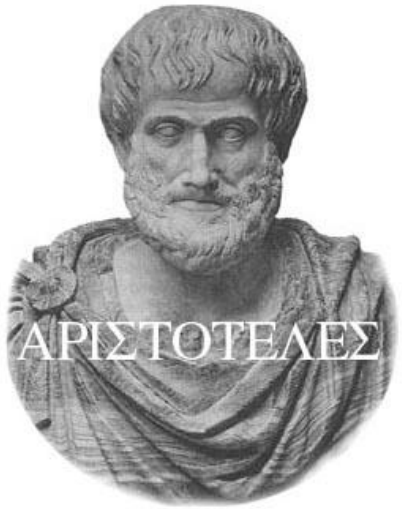
ENABLING TECHNOLOGIES FOR PROCESS INNOVATION AND INTENSIFICATION

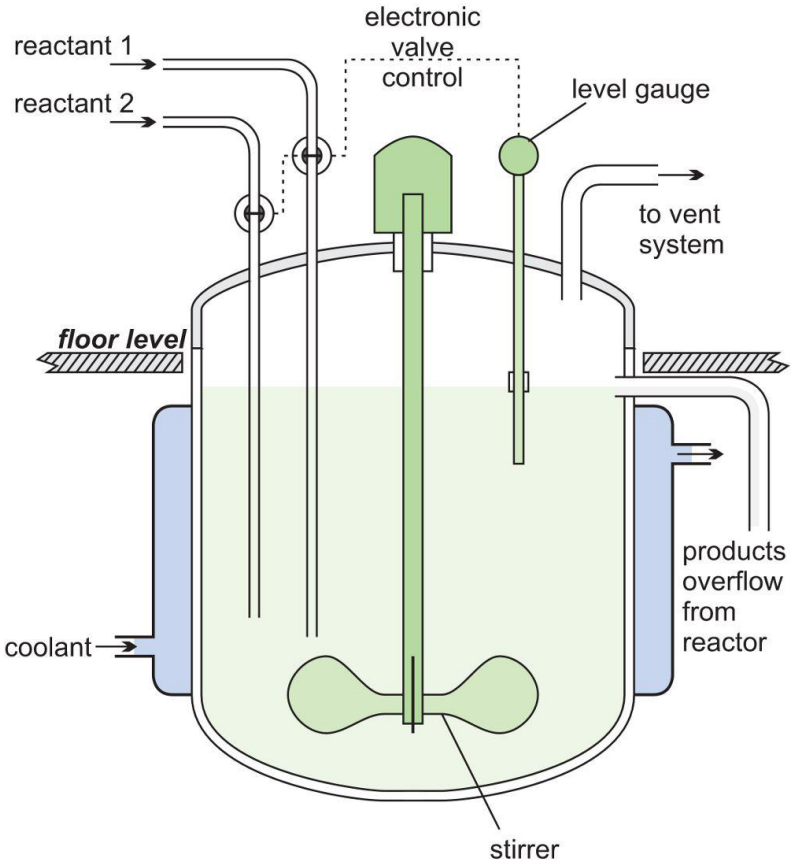
- MICROWAVES
- CAVITATIONAL TURBINE REACTORS
- BALL MILLING
- HIGH PRESSURE REACTIONS
- SFE-CO_2, SUB-CRITICAL H_2O, LIQ. BUTANE REACTORS
- PHOTOCHEMISTRY
- MICRO- & MESO-CHANNELS FLOW-REACTORS
- COMBINED ULTRASOUND MICROWAVES
- HIGH-SHEAR MIXERS TURBO-REACTORS
- HYDRODYNAMIC CAVITATION
- ULTRASOUND

CONVENTIONAL HEATING & STIRRING

Corpora non agunt nisi fluida seu soluta !!!







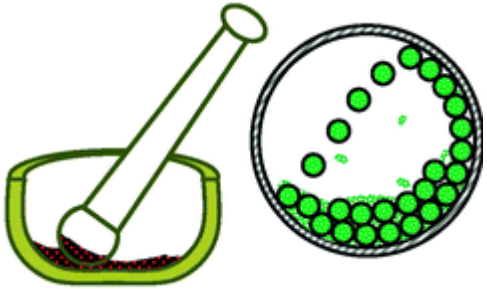
MOST CHEMISTS ARE EXTREMELY CONSERVATIVE!

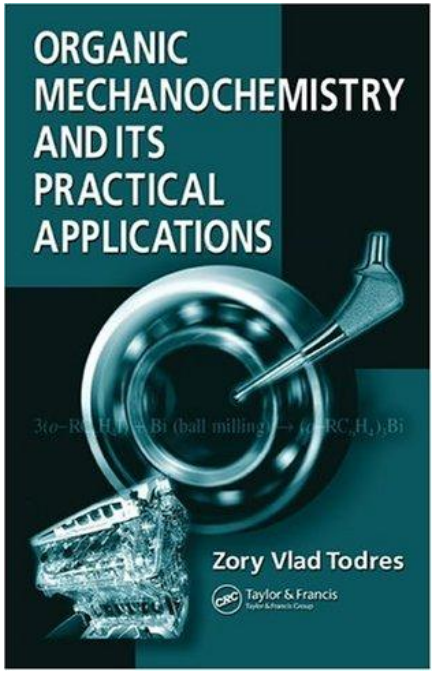
Scientific and technological progress now happens at the interfaces between two or more scientific and technical disciplines and Chemistry overlaps with almost all scientific domains

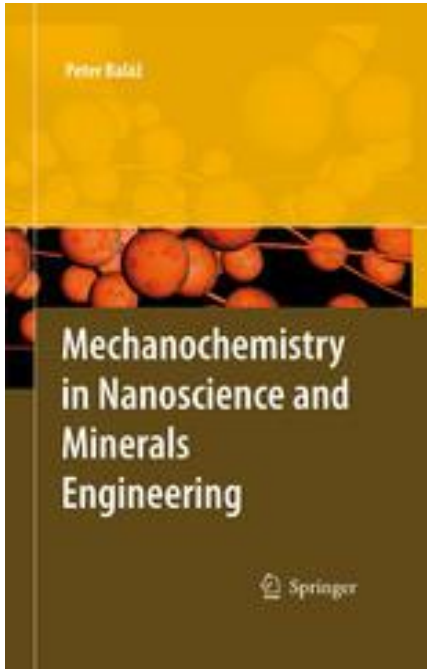
In spite of the multidisciplinary interaction of Chemistry, most of the chemists are extremely conservative in the design of their synthetic protocols

MECHANOCHEMISTRY

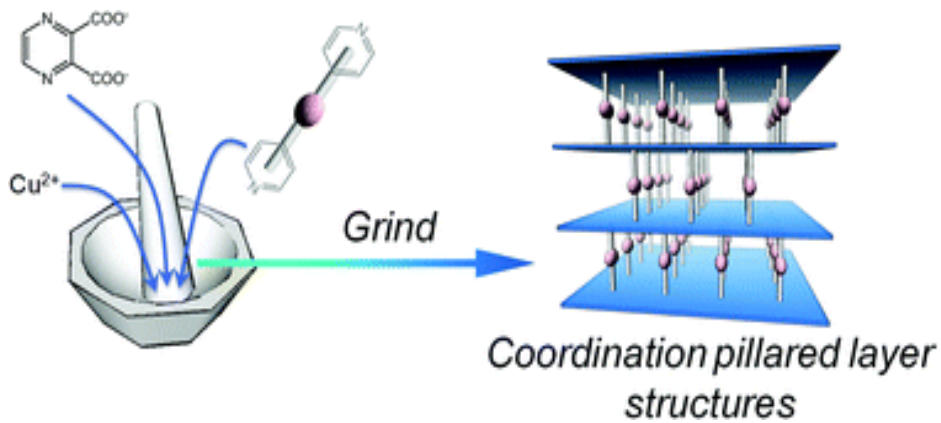
The application of mechanical force to chemical systems, either in the form of mechanical grinding and milling, or in the form of ultrasound has resulted in a number of recent exciting developments and practical achievements that opened the door to modern mechanochemical research in the field of nanomaterials





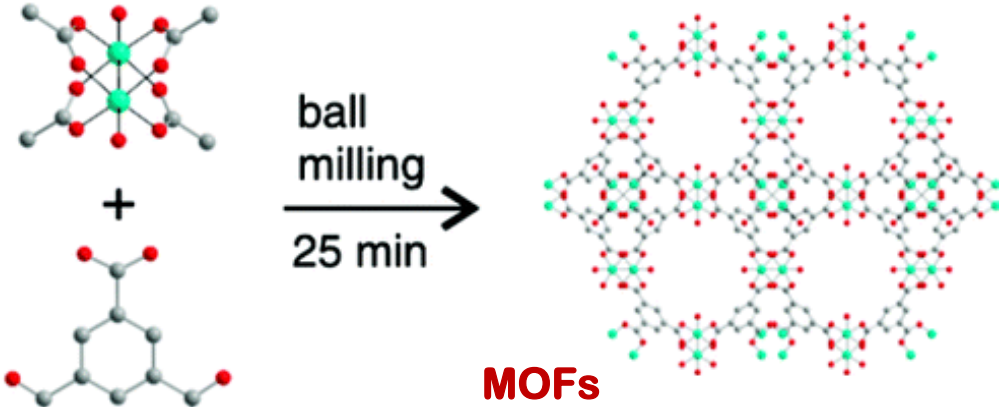


“ ORDER IN THE CAOS ”



Porous coordination polymers by grinding

- *Dalton Trans.*, **2012,** *41*, 3956-3961



- *Chem. Mater.*, **2010**, *22* (18), pp 5216–5221

Chem Soc Rev

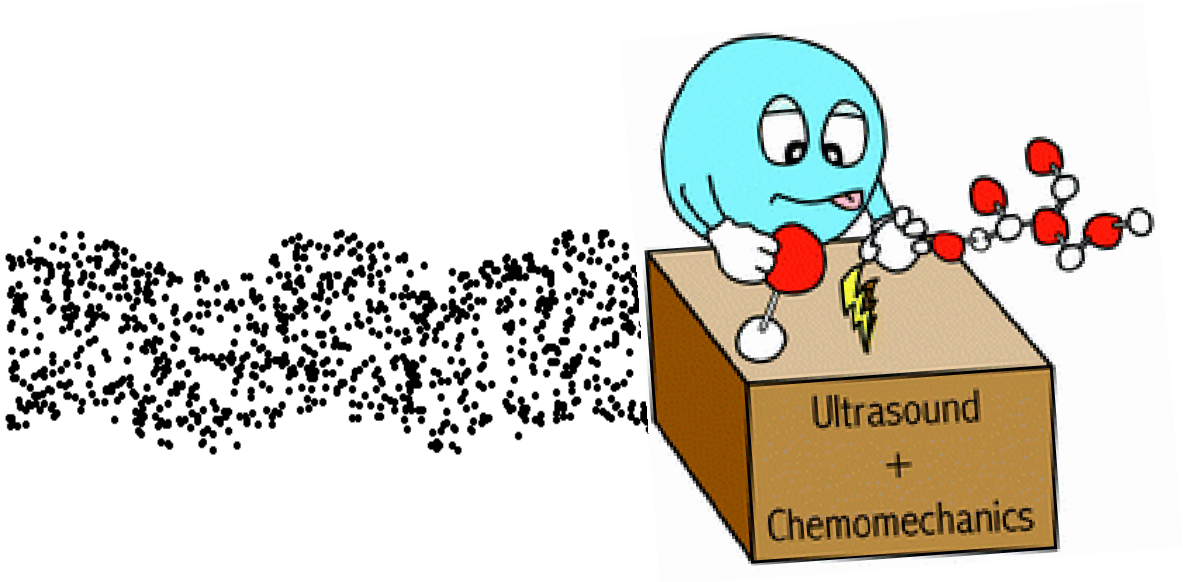
RSC Publishing

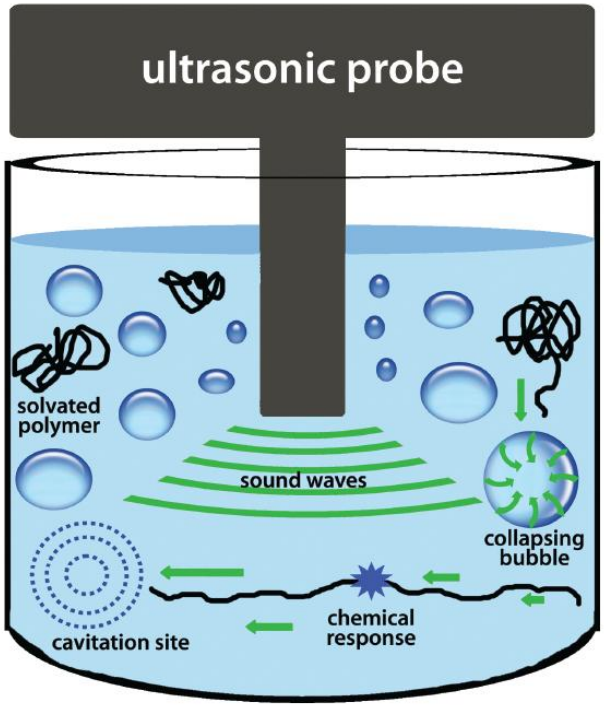
TUTORIAL REVIEW

On the mechanochemical activation by ultrasound

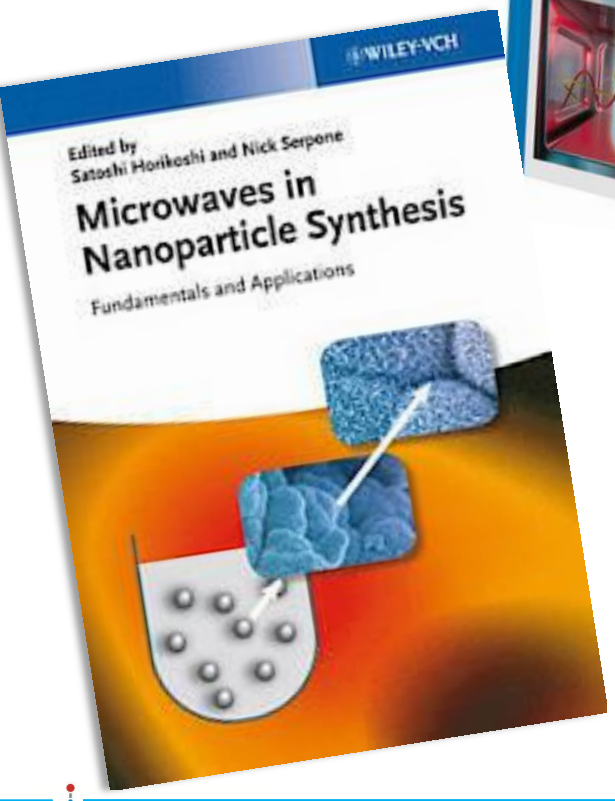
Giancarlo Cravotto,*[a] Emanuela Calcio Gaudino[a] and Pedro Cintas*[b]

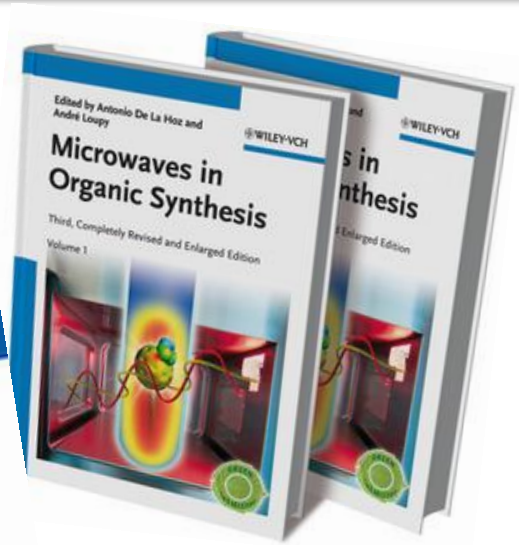
Chem. Soc. Rev., **2013**, *42*, 7521

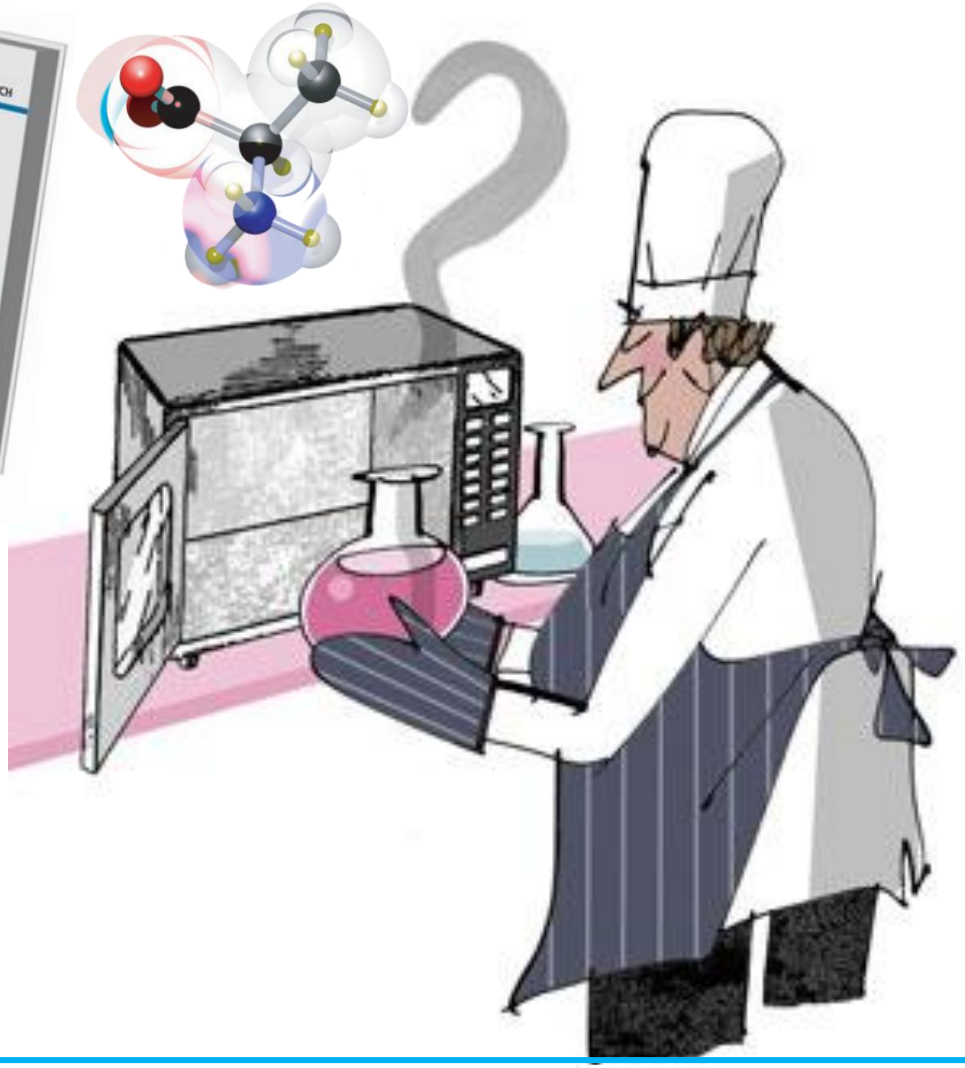




MICROWAVE TECHNOLOGY IN NANOMATERIALS PREPARATION



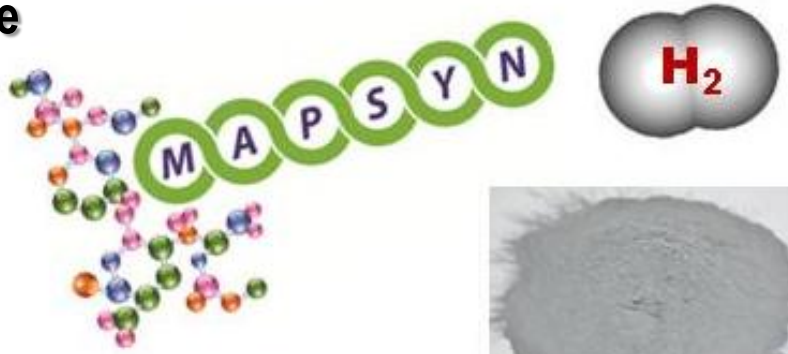




SEVENTH FRAMEWORK PROGRAMME

MAPSYN

Development of alternative energy powered chemical reactions



"selective hydrogenations"

Chem. Eng. Process. **2013**, *71*, 19-30

Contents lists available at SciVerse ScienceDirect

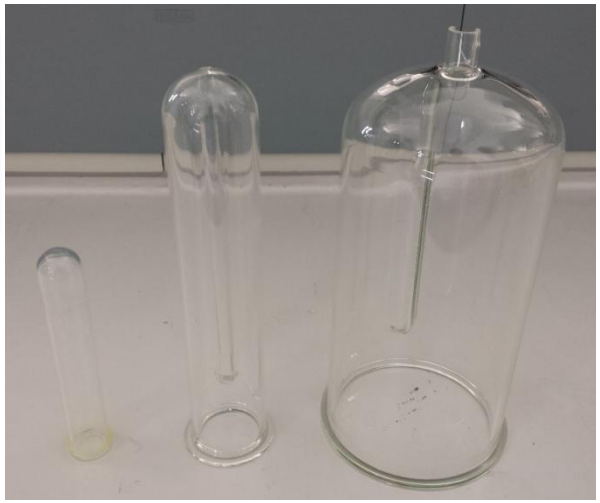
Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

V. Hessel[a,*], G. Cravotto[b], P. Fitzpatrick[c], B.S. Patil[a], Jüergen Lang[d], Werner Bonrath[e]

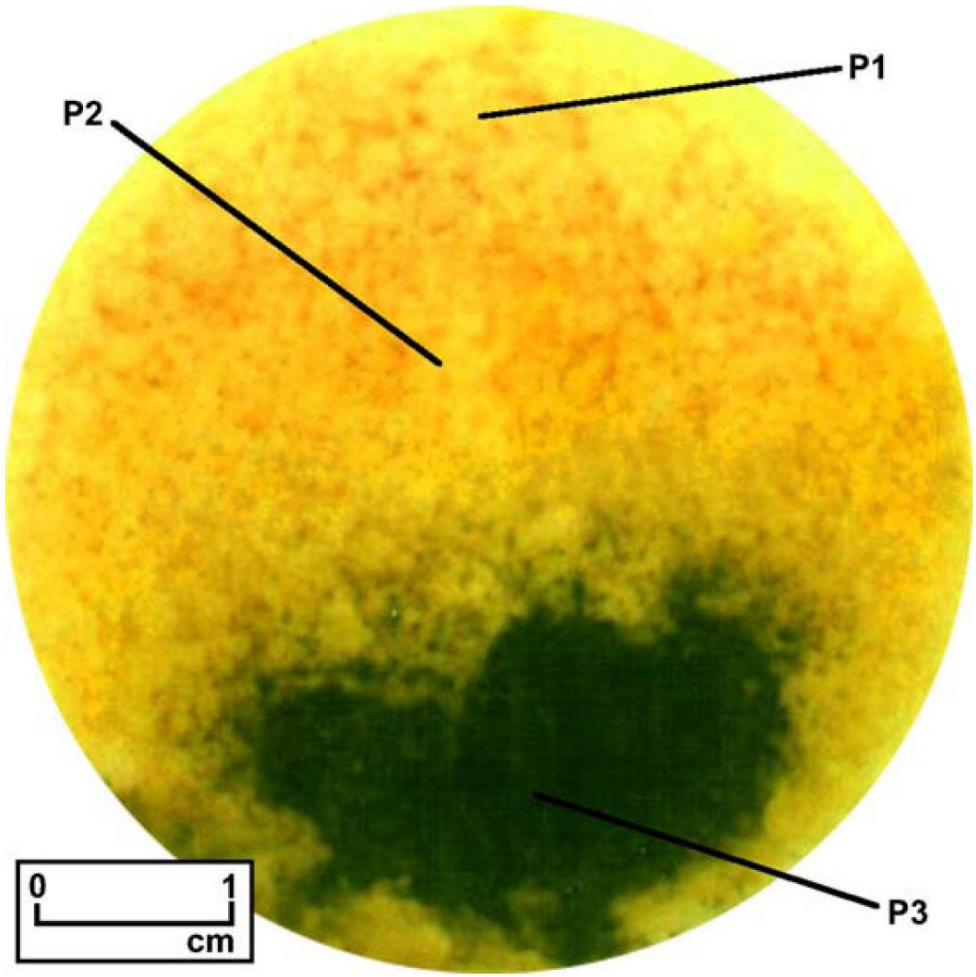
Industrial applications of plasma, microwave and ultrasound techniques: Nitrogen-fixation and hydrogenation reactions

MW-ASSISTED SOLID-PHASE GRAFTING AND COATING



Thermal heterogeneity under MW irradiation for solventless solid–liquid phase-transfer catalytic (PTC) reactions by means of a thermovision camera and fiber-optics thermometer

Area	(°C)	(%)	(%)
P1	70	100	0
P2	125	55	45
P3	200	0	100



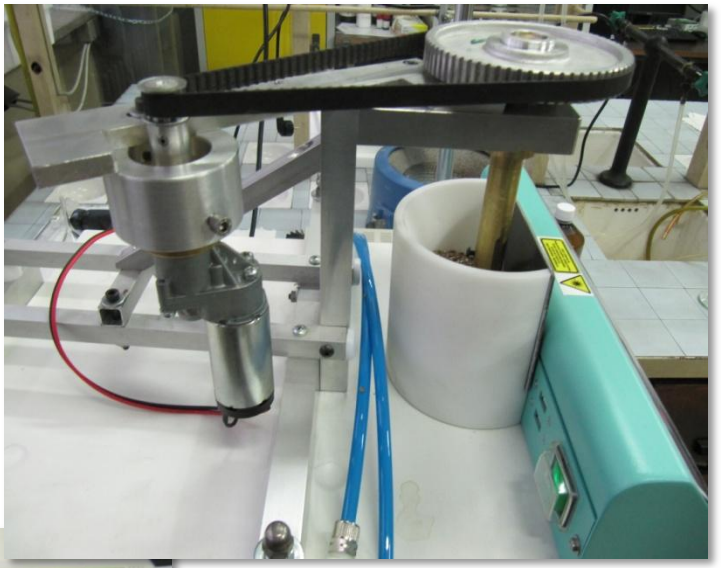
Bogdal, D.; Bednarz, S.; Lukasiewicz, M., *Tetrahedron* ***2006,*** *62, (40), 9440-9445.*

ARCHIMEDEAN SCREW FOR SOLVENTLESS FLOW-REACTIONS

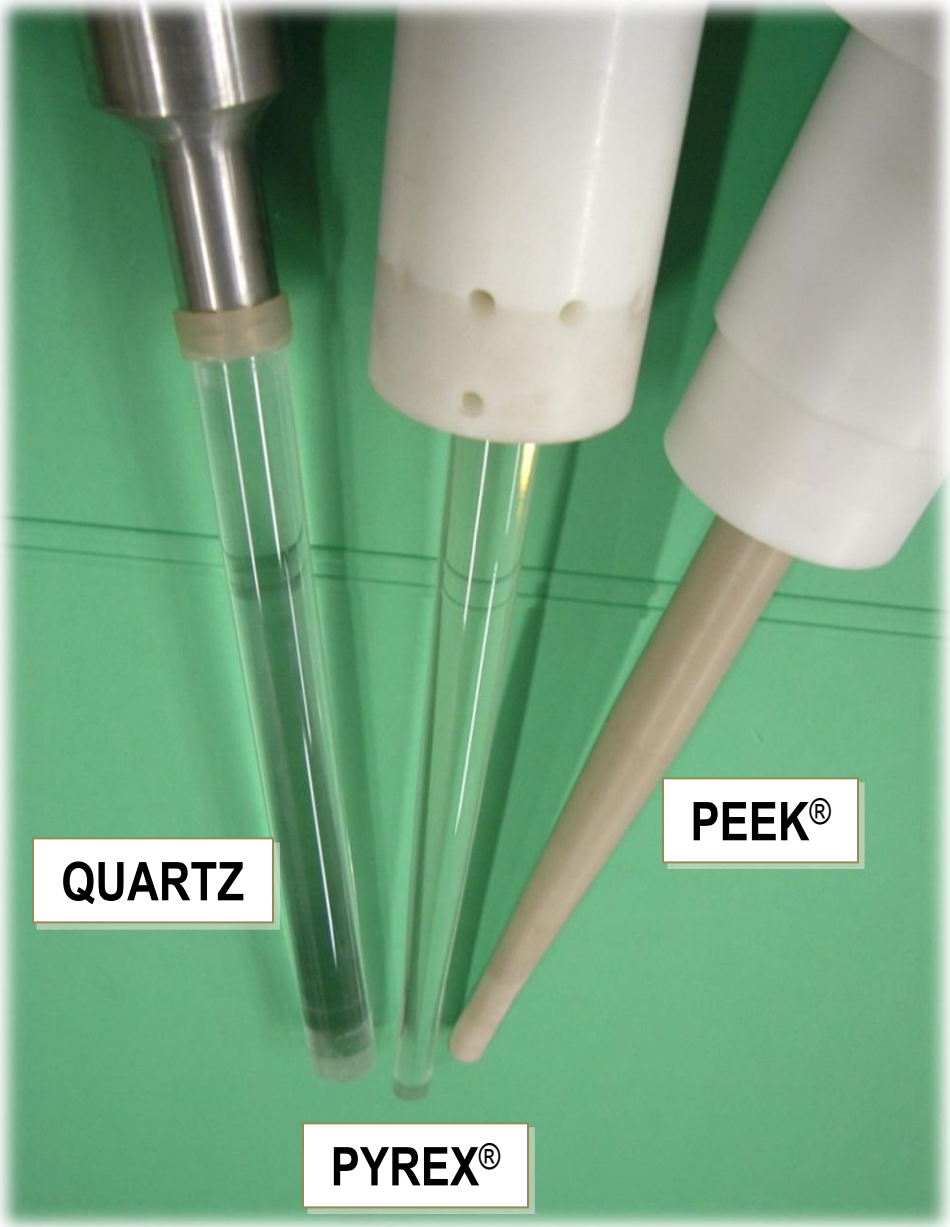
HOMOGENEOUS IRRADIATION OF REAGENTS AT THE SOLID-STATE

THE REACTING MIXTURE CAN MELT DURING THE IRRADIATION


NEOS-GR
Microwave Gravity Station




DC POWER SUPPLY
0.66
Amp
08.2
Volt



Chem Soc Rev

Chemical Society Reviews

www.rsc.org/chemsocrev

Volume 35 | Number 2 | February 2006 | Pages 117 – 200

ISSN 0306-0012

RSC Publishing

CRITICAL REVIEW

Giancarlo Cravotto and Pedro Cintas

Power ultrasound in organic synthesis: moving cavitational chemistry from academia to innovative and large-scale applications

nature protocols
Recipes for Researchers

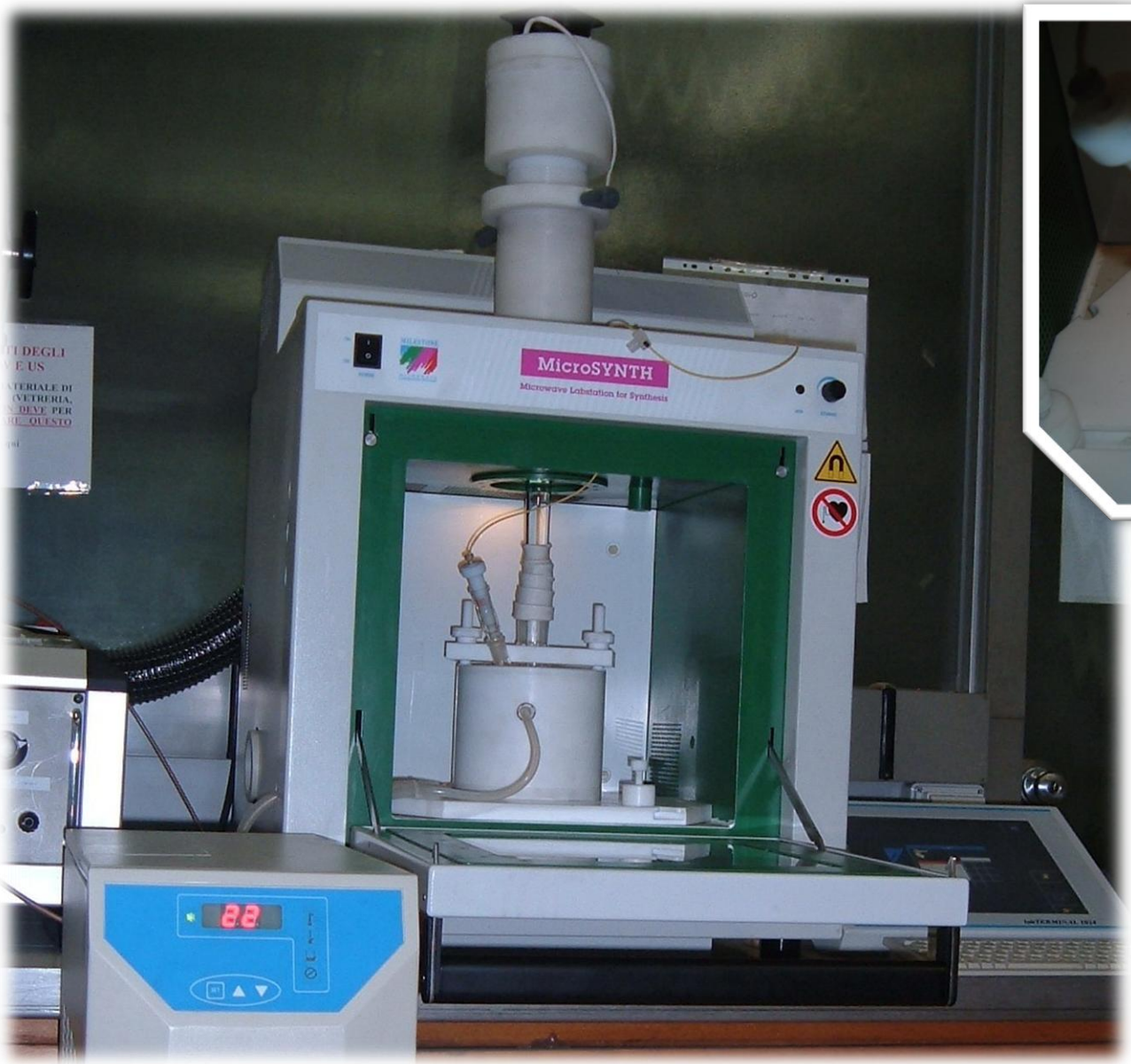
NATURE PROTOCOLS | VOL.5 NO.3 | 2010 | 607

PROTOCOL

Alkyne–azide click reaction catalyzed by metallic copper under ultrasound

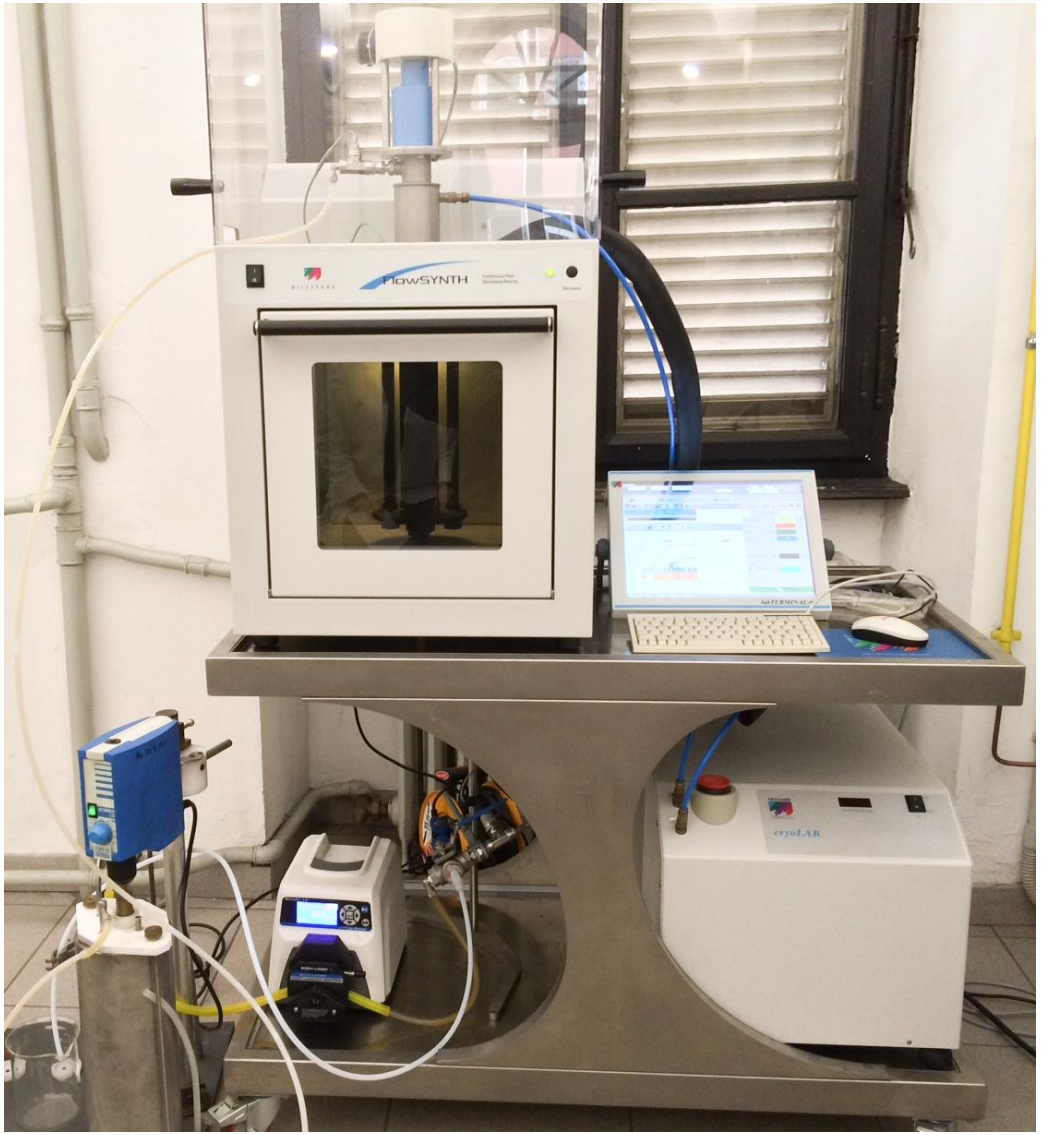
Pedro Cintas[1], Alessandro Barge[2], Silvia Tagliapietra[2], Luisa Boffa[2] & Giancarlo Cravotto[2]

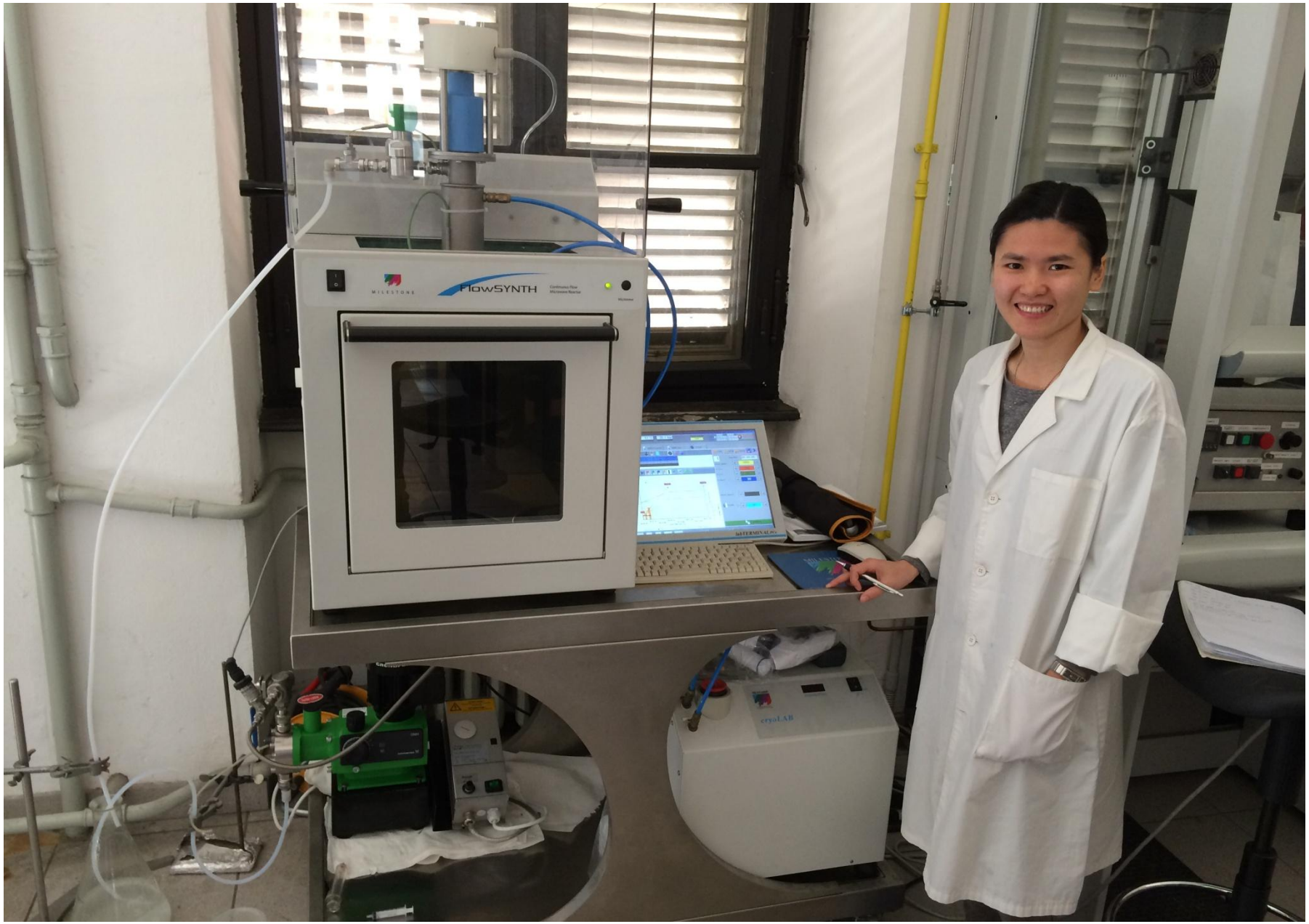
nature publishing group npg


MicroSYNTH
Microwave Labstation for Synthesis


A TUTTI GLI UTENTI DEGLI
STRUMENTI MW E US
SI FA PRESENTE CHE IL MATERIALE DI
QUESTO LABORATORIO (VETRERIA,
CONSUMABILE ECC...) NON DEVE PER
NESSUN MOTIVO LASCIARE QUESTO
LOCALE.
MicroSYNTH
Microwave Lobstation for Synthesis

FLOW-MW REACTOR




MILESTONE
FlowSYNTH
cryoLAB

ACS Sustainable Chemistry & Engineering

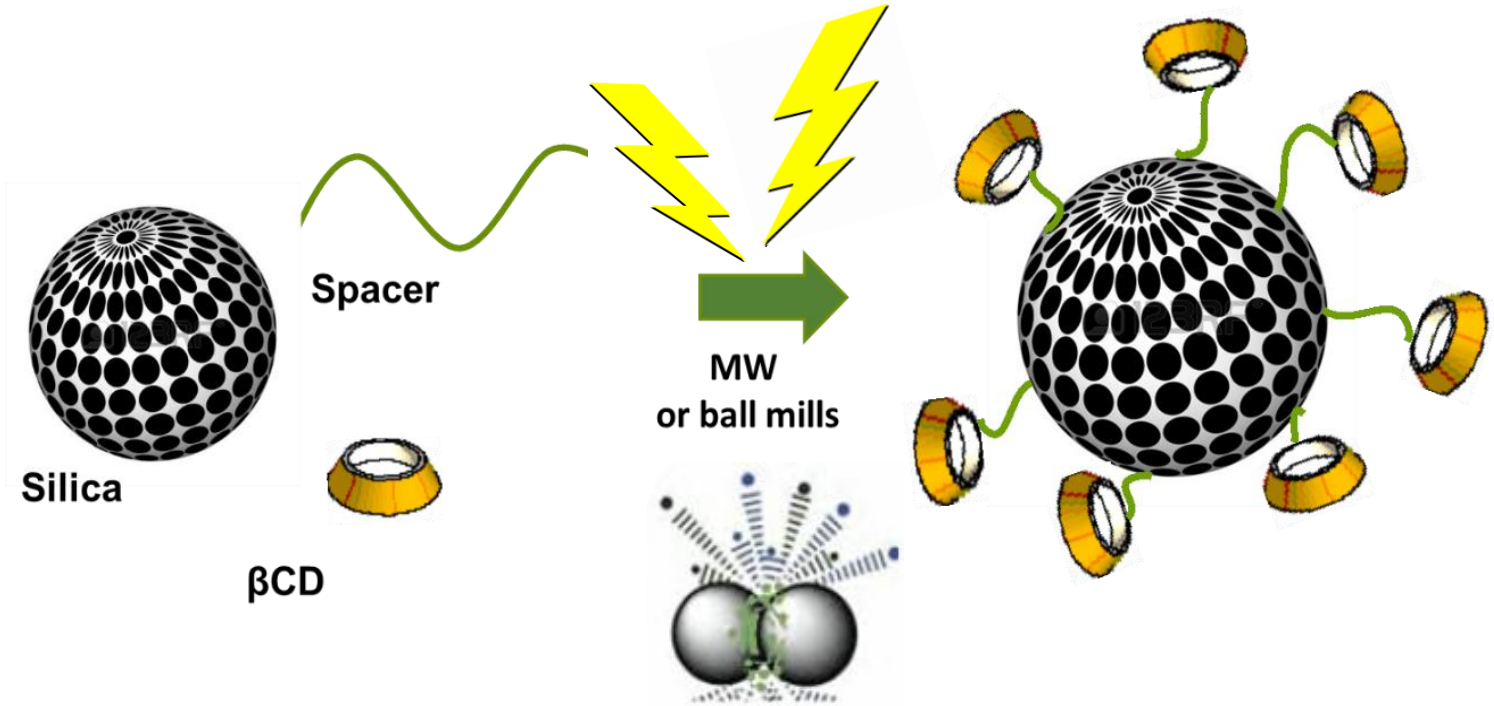
DOI: 10.1021/sc500546e

Research Article

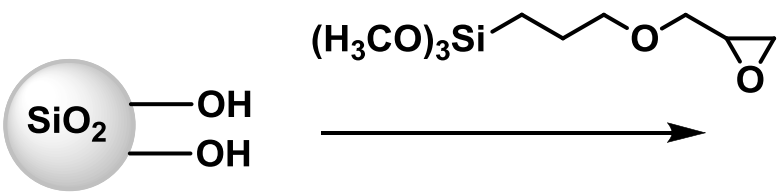
pubs.acs.org/journal/ascecg

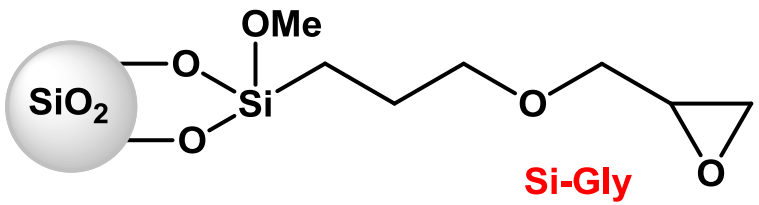
Efficient Green Protocols for Preparation of Highly Functionalized β-Cyclodextrin-Grafted Silica

Katia Martina,[†] Francesca Baricco,[†] Gloria Berlier,[‡] Marina Caporaso,[†] and Giancarlo Cravotto*[,†]

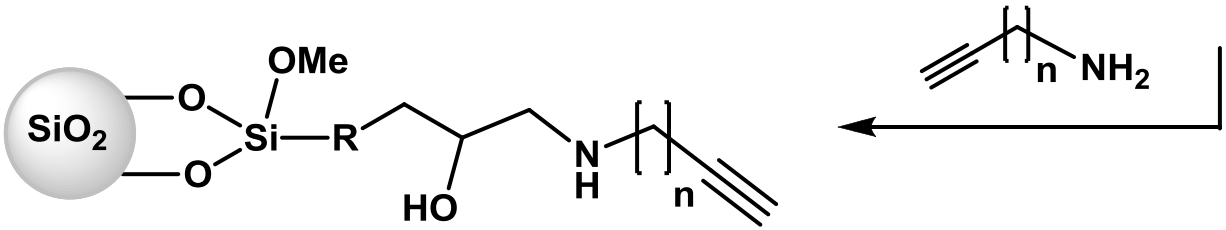


SYNTHETIC SCHEME

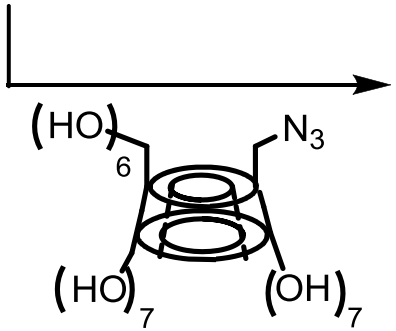


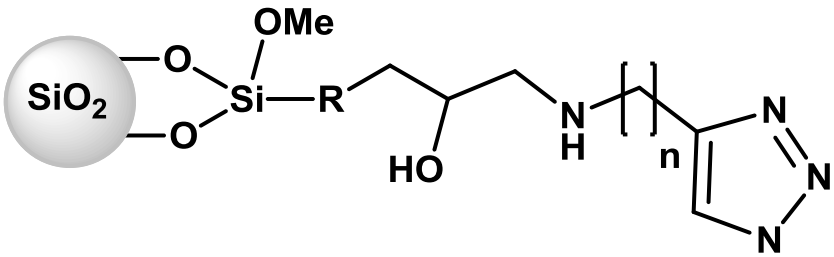


Si-Gly

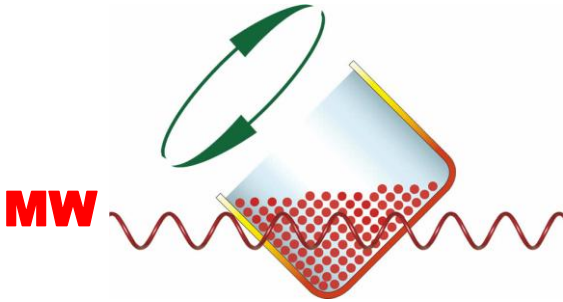


Si-Gly-Und



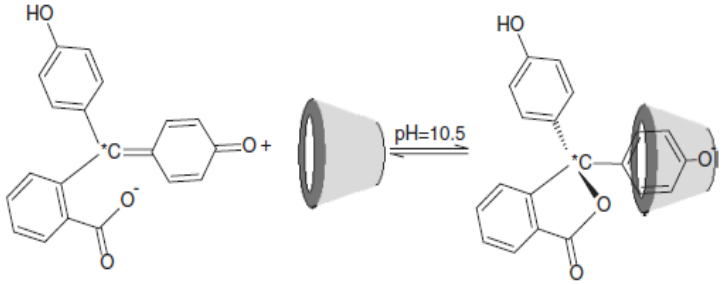


Si-Gly-Und-CD



RotoSYNTH ®

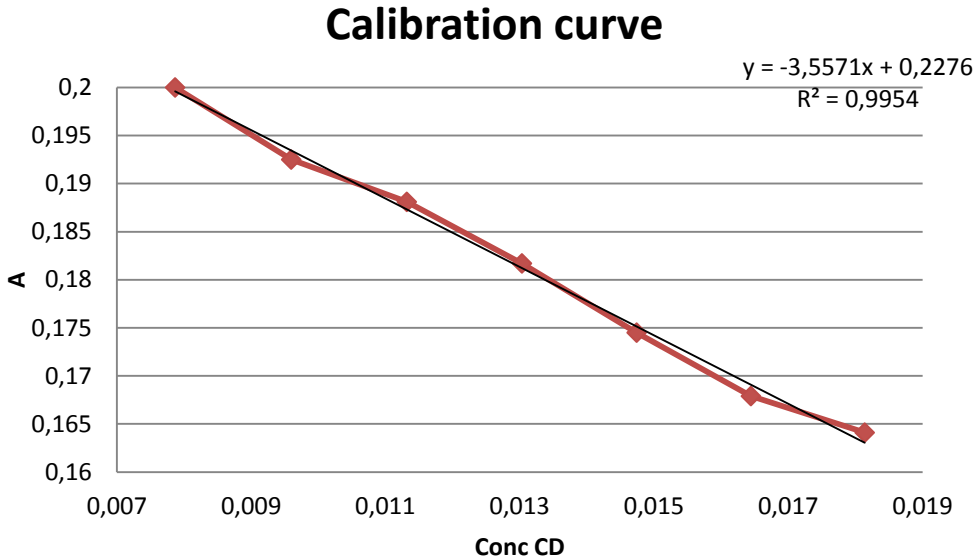
CD quantification (Phenolphtalein)



CD (colorless) + PHP (red)

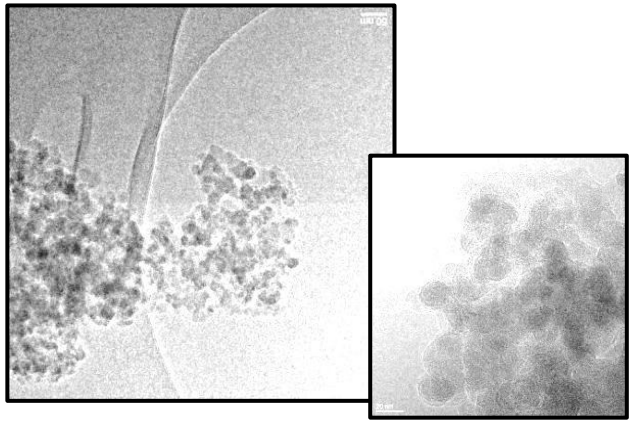
↓↑

CD-PHP complex (colorless)

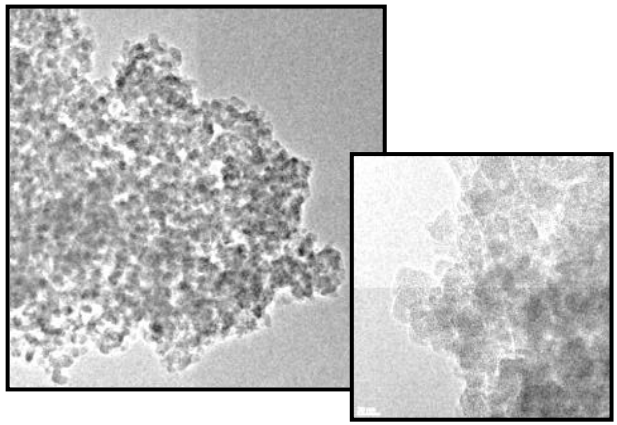


TEM analysis

Si-Gly-Und-βCD - MW



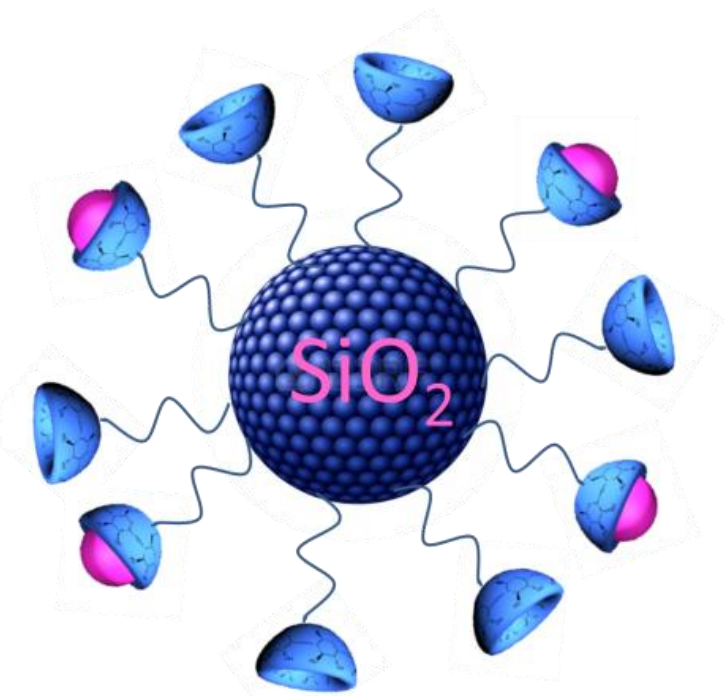
Si-Gly-Und-βCD - Ball Mill

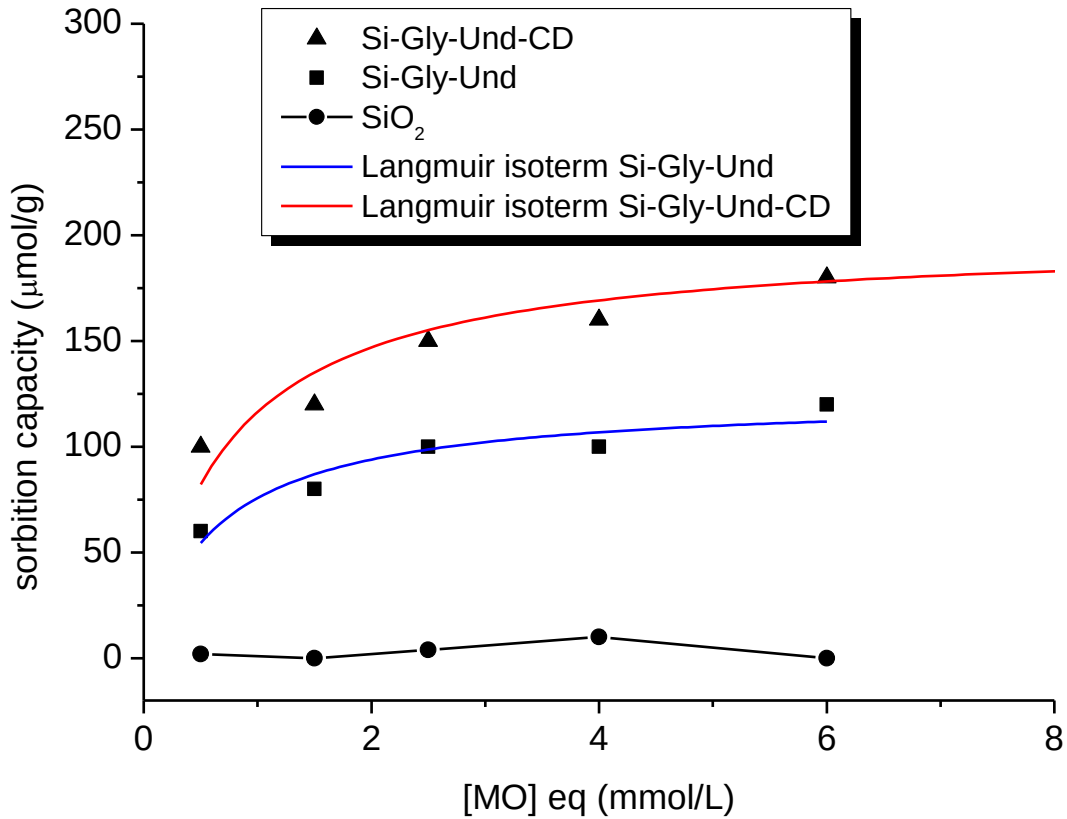


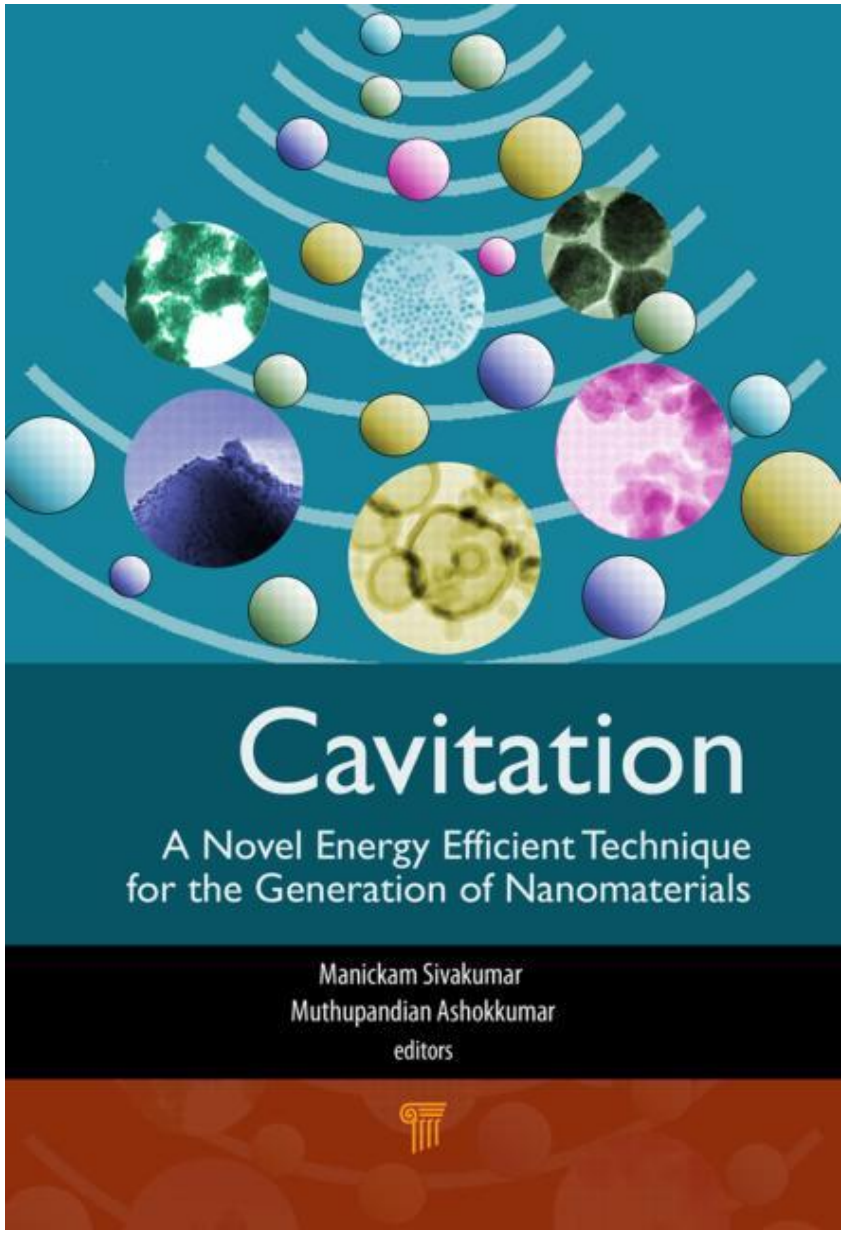
Sorption Capacity

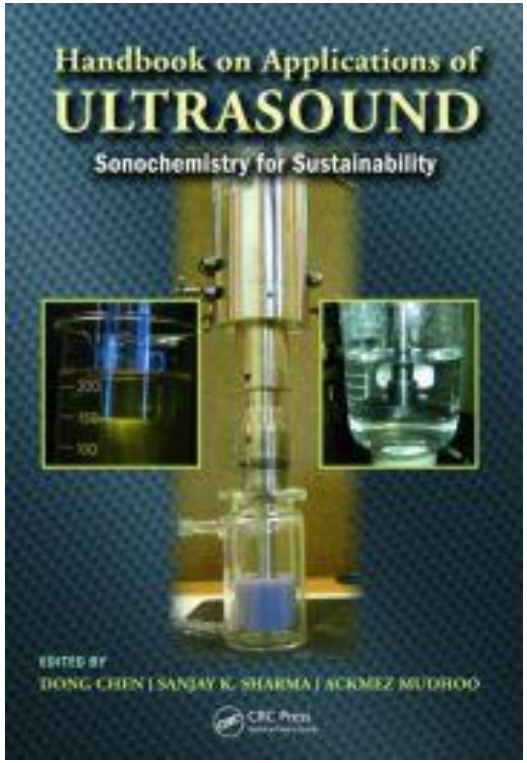
Langmuir Isotherm

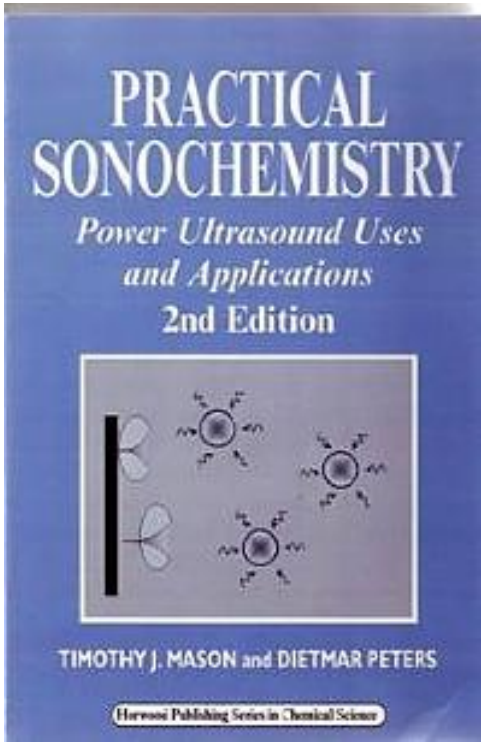
$Q_{ads}=(Q_m*K_l*[MO]_{eq})/(K_l*[MO]_{eq}+1)$

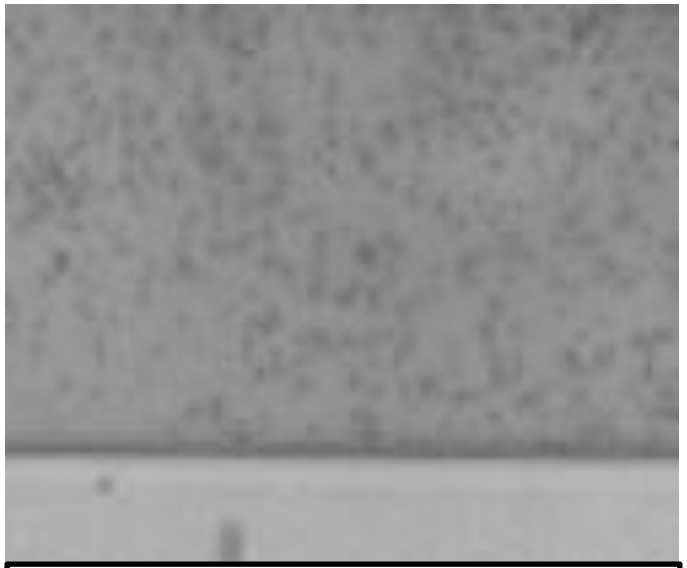




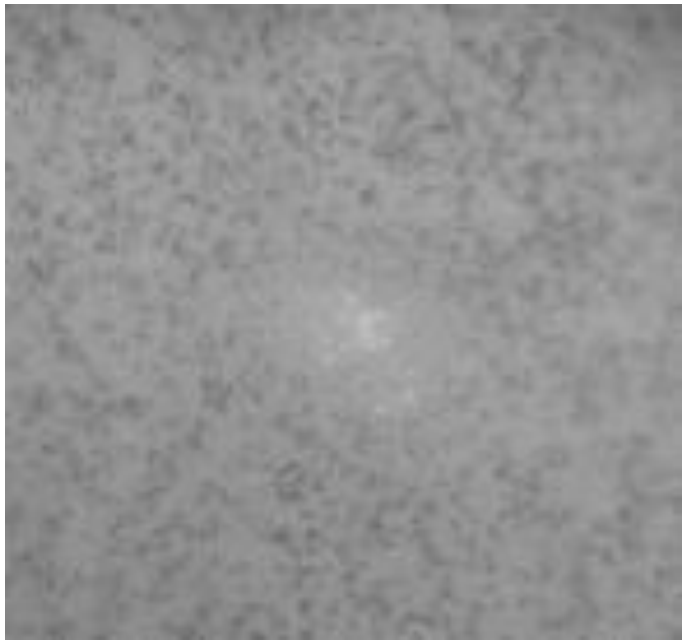

Cavitation
A Novel Energy Efficient Technique for the Generation of Nanomaterials
Manickam Sivakumar
Muthupandian Ashokkumar
editors

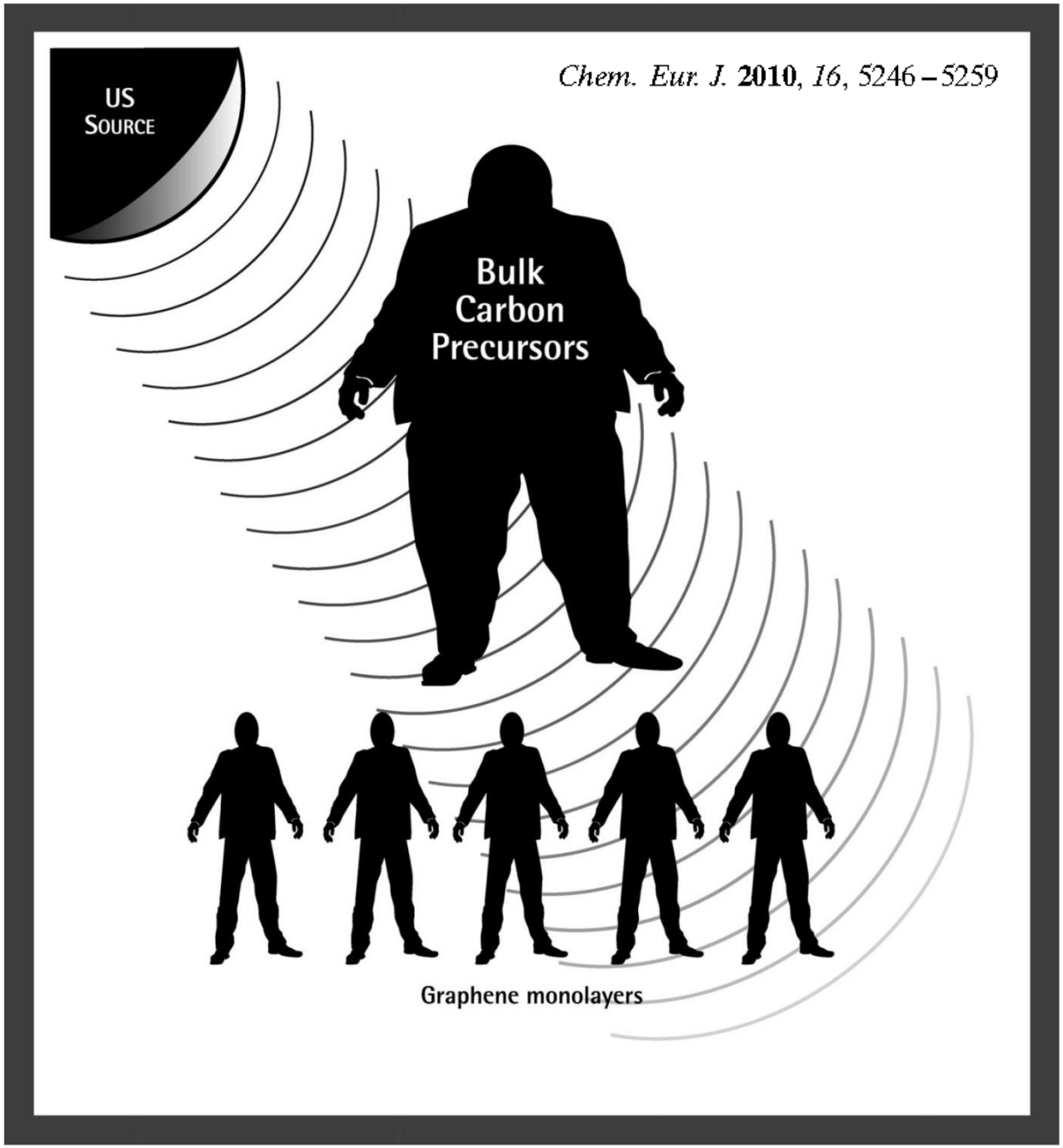

Handbook on Applications of
ULTRASOUND
Sonochemistry for Sustainability
EDITED BY
DONG CHEN | SANJAY K. SHARMA | ACKMEZ MUDHOO
CRC Press


PRACTICAL
SONOCHEMISTRY
Power Ultrasound Uses and Applications
2nd Edition
TIMOTHY J. MASON and DIETMAR PETERS
Horwood Publishing Series in Chemical Science



Video courtesy of University of Twente, Netherlands. and Shimadzu Europa GmbH, Duisburg, Germany



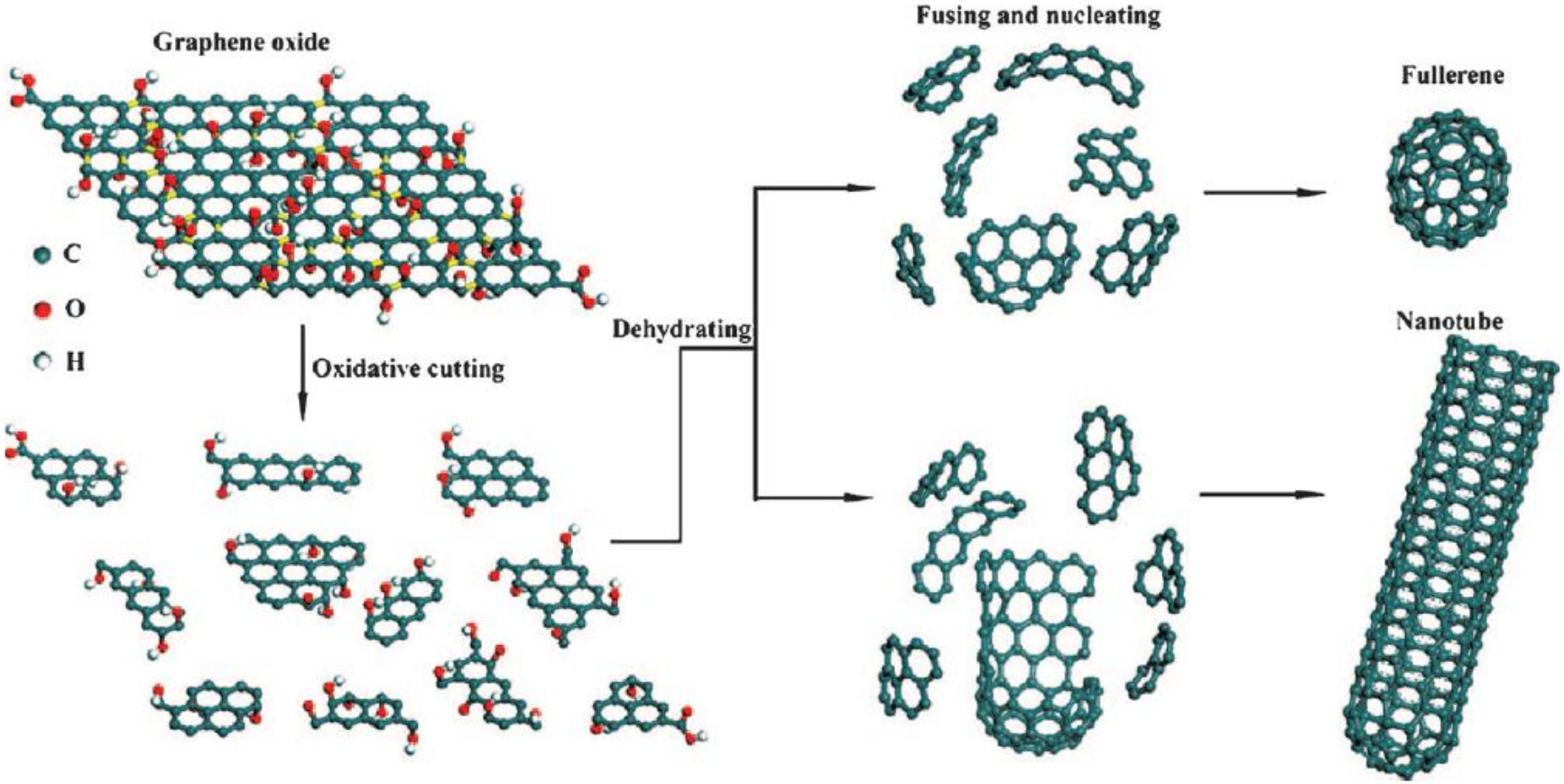


CHEMISTRY
A EUROPEAN JOURNAL

Chem. Eur. J. **2010**, *16*, 5246 – 5259

Sonication-Assisted Fabrication and Post-Synthetic Modifications of Graphene-Like Materials

Giancarlo Cravotto*[a] and Pedro Cintas*[b]



www.rsc.org/njc Cite this: *New J. Chem.*, 2011, **35**, 915–919 **PAPER**

Rapid purification/oxidation of multi-walled carbon nanotubes under 300 kHz-ultrasound and microwave irradiation

Giancarlo Cravotto,*[ab] Davide Garella,[a] Emanuela Calcio Gaudino,[a] Francesco Turci,[bc] Serena Bertarione,[c] Giovanni Agostini,[c]

LETTER 1459

SYNLETT 2012, 23, 1459–1462

Functionalization of Single-Walled Carbon Nanotubes through 1,3-Cyclo-addition of Carbonyl Ylides under Microwave Irradiation

Silvia Tagliapietra,[a] Giancarlo Cravotto,*[a] Emanuela Calcio Gaudino,[a] Sonja Visentin,[a] Valentina Mussi[b]

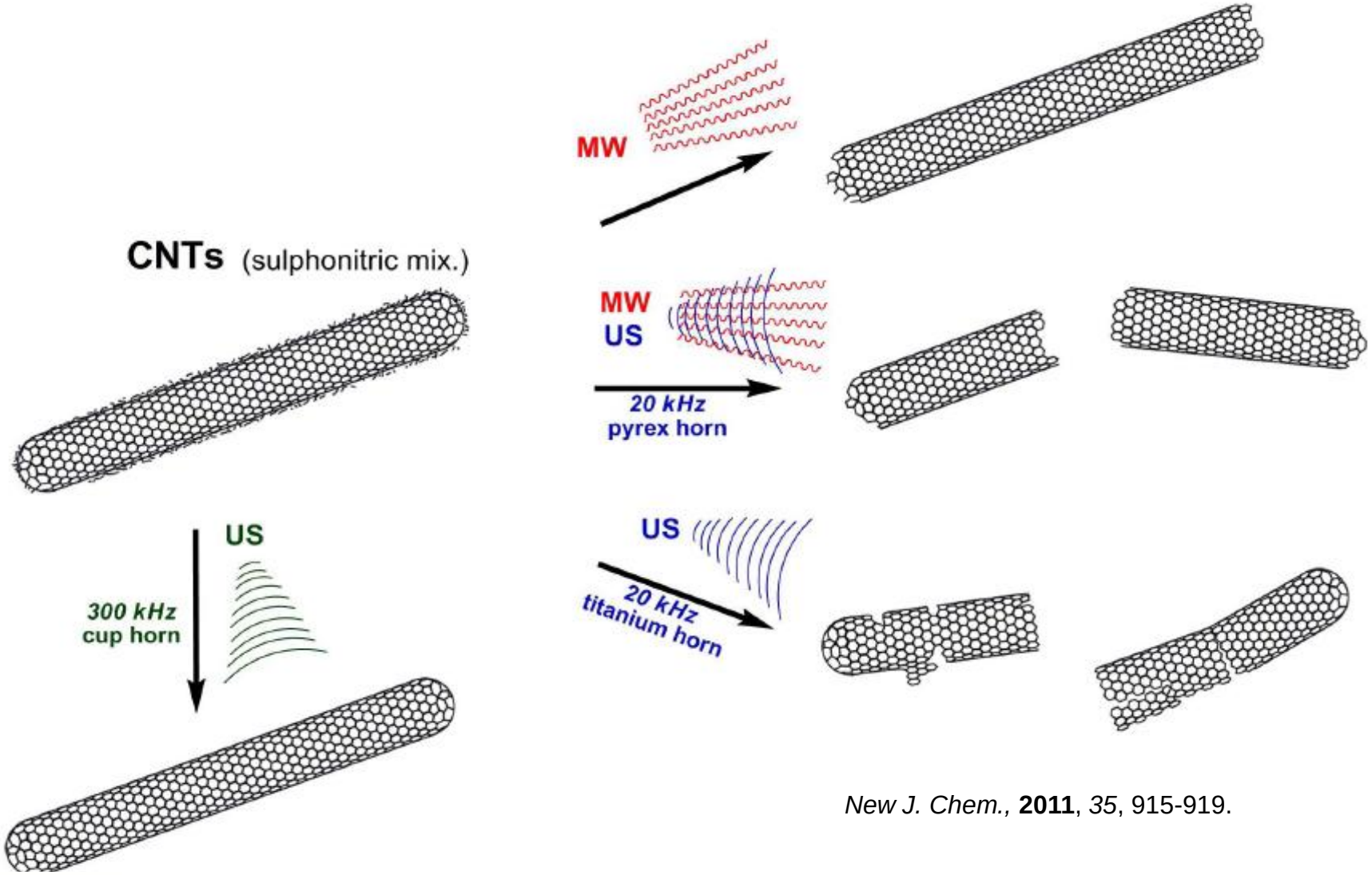
Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 4708

A novel SWCNT platform bearing DOTA and β-cyclodextrin units. "One shot" multidecoration under microwave irradiation†

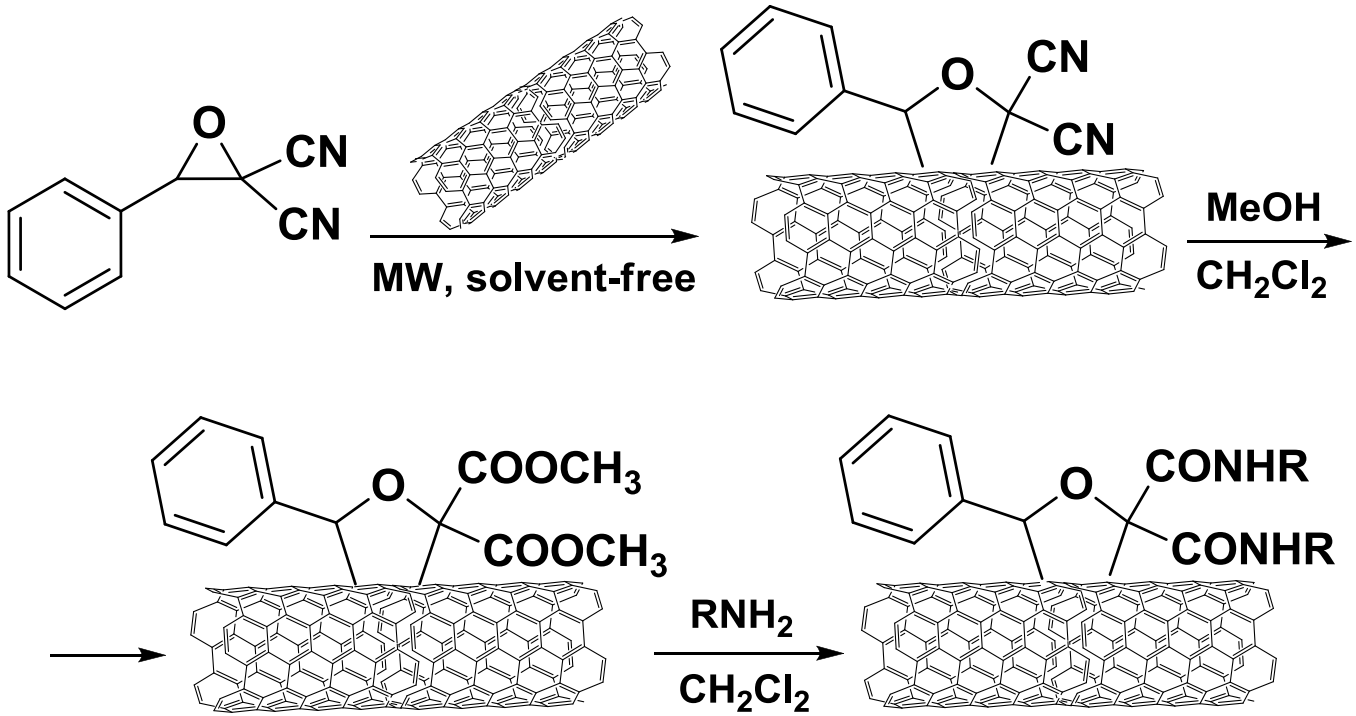
E. Calcio Gaudino,[a] S. Tagliapietra,[a] K. Martina,[a] A. Barge,[a] M. Lolli,[a] E. Terreno,[b] D. Lembo[c] and G. Cravotto*[a]

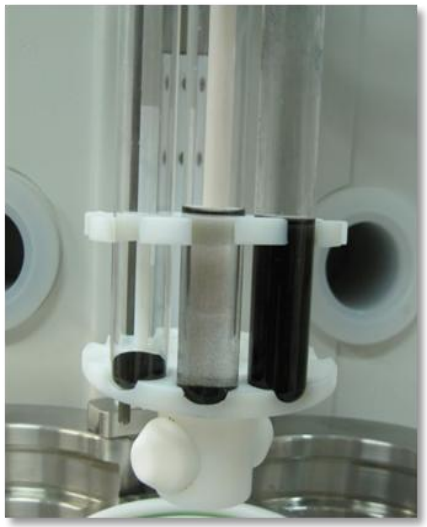
Rapid purification/oxidation of MWCNTs

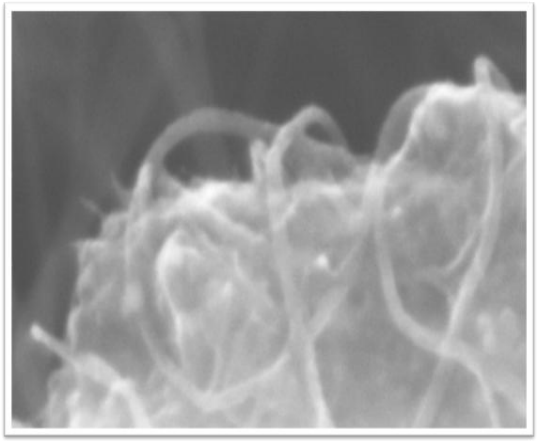


New J. Chem., **2011**, *35*, 915-919.

SWCNTs FUNCTIONALIZATION under MW

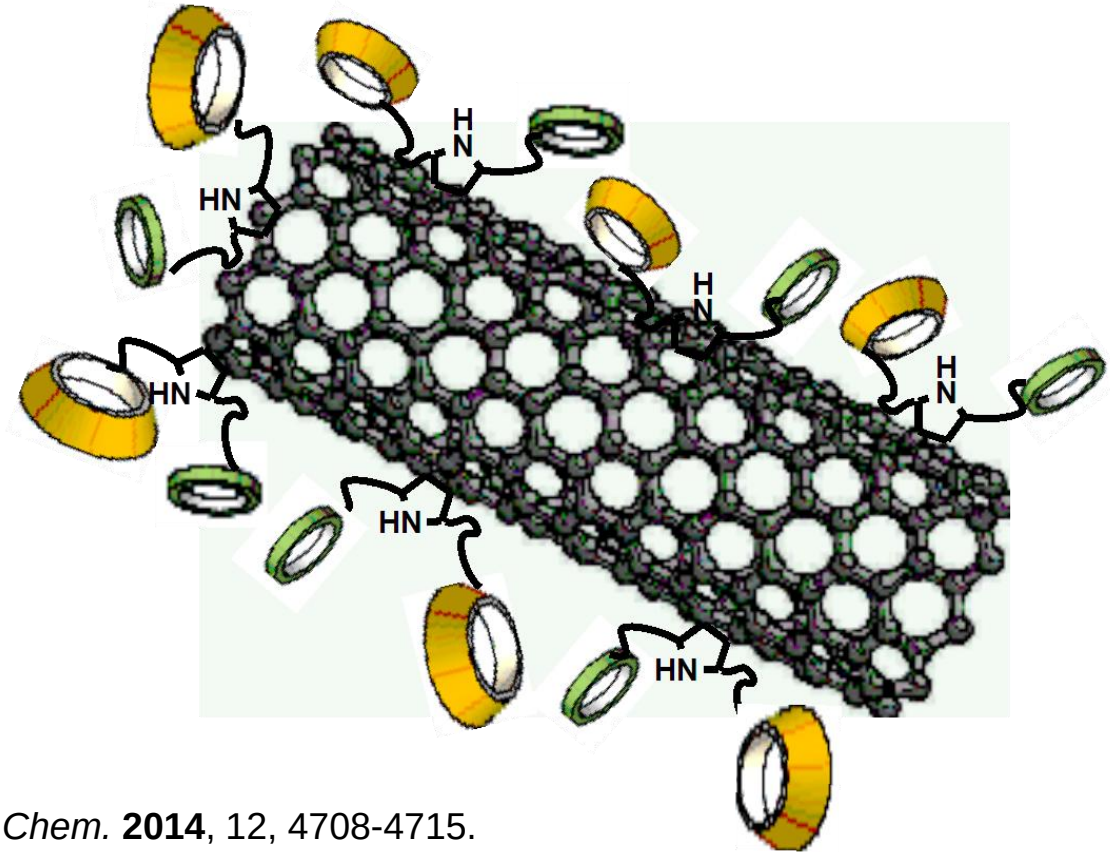


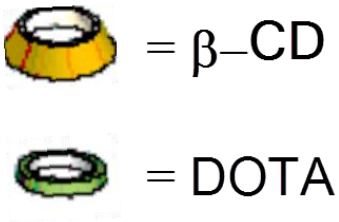




Synlett **2012**, *23*, 1459-1462

MW-assisted synthesis of SWCNTs platform bearing DOTA and β-cyclodextrin

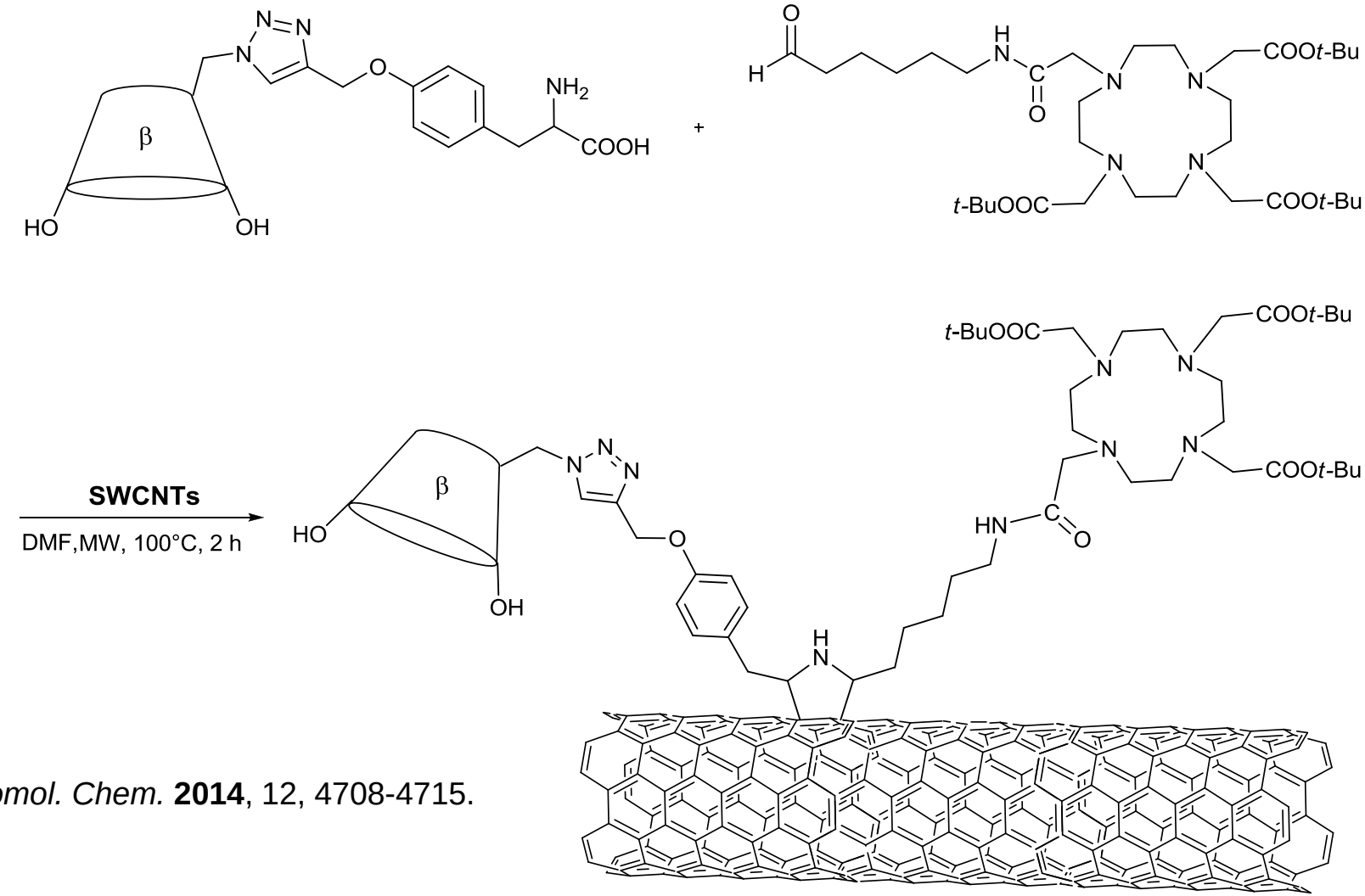




Org. Biomol. Chem. **2014**, 12, 4708-4715.

DOTA (1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid

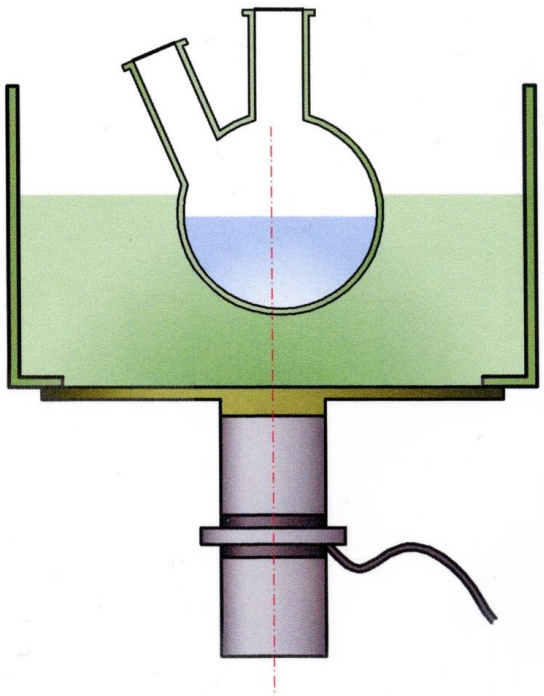
SWCNTs – DOTA - β-cyclodextrin



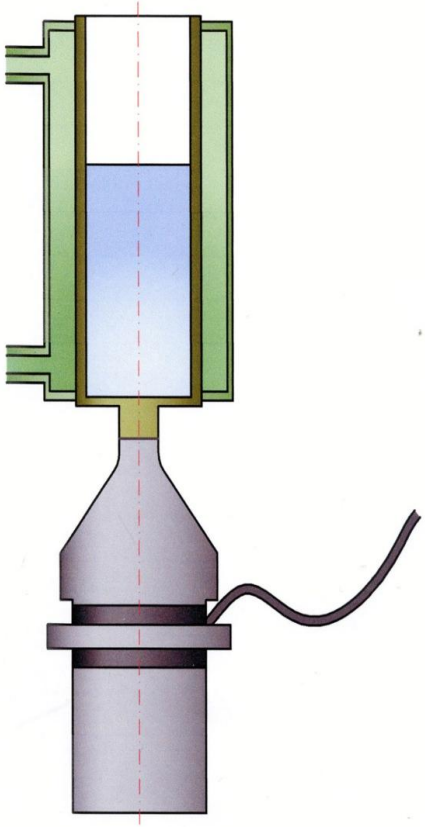
Org. Biomol. Chem. **2014**, 12, 4708-4715.

HIGH-POWER ULTRASONIC PROBES

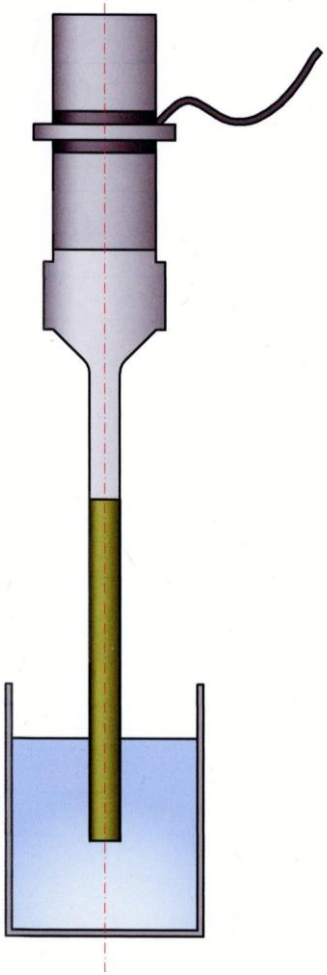
CUP HORN
BATH



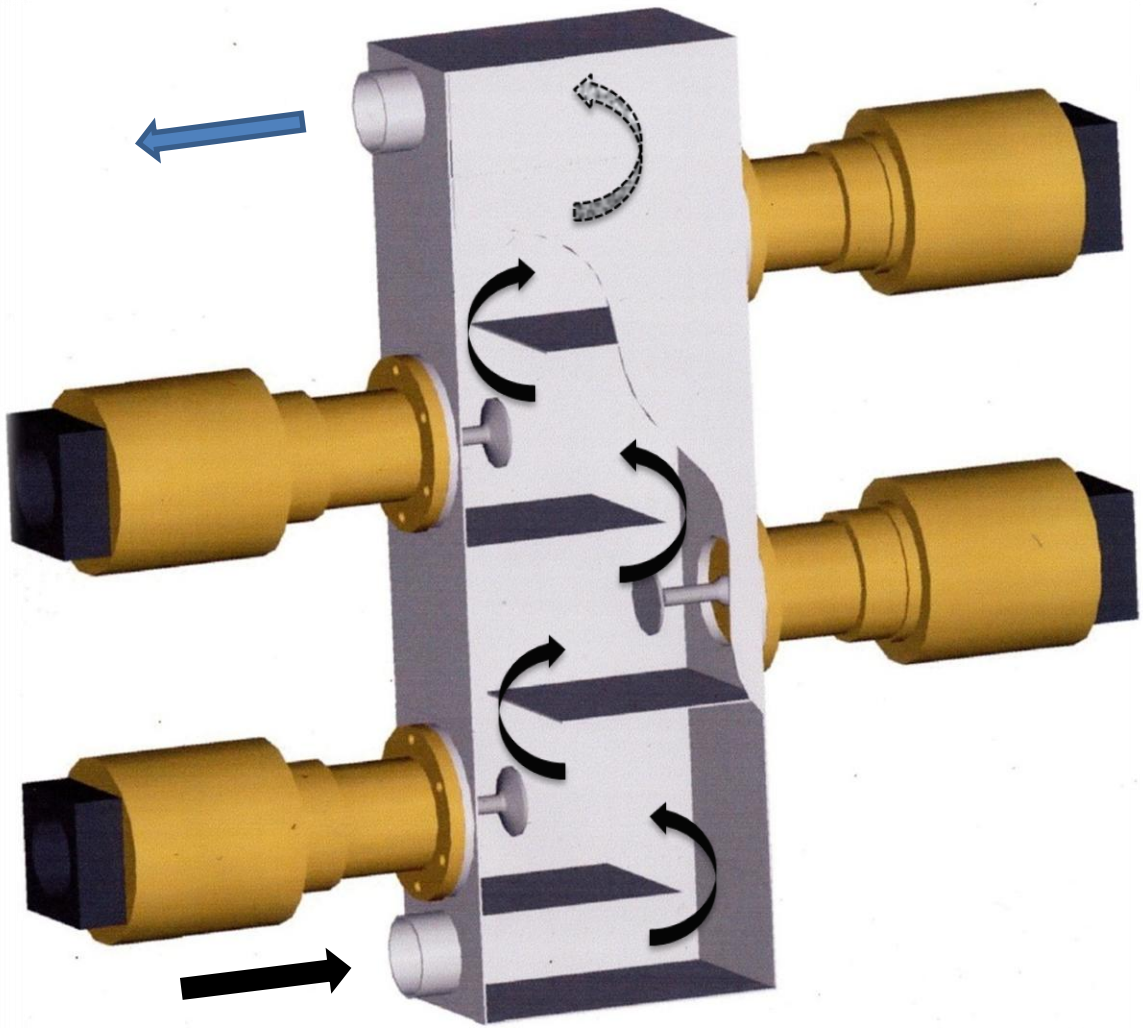
CAVITATING
TUBE

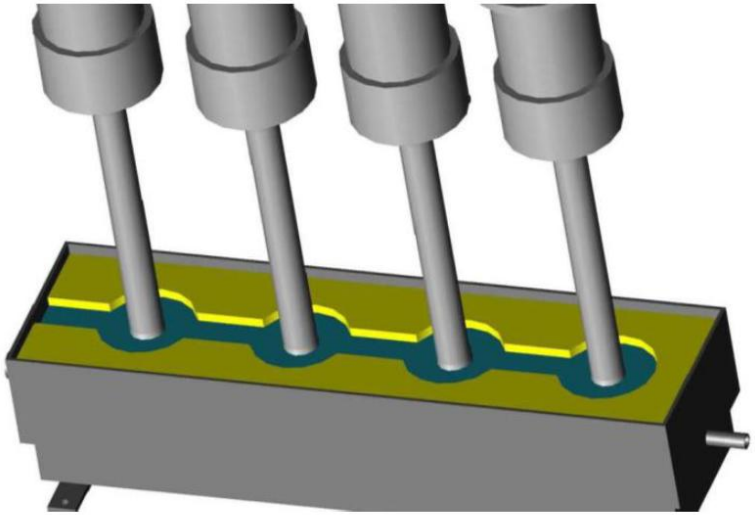


IMMERSION HORN

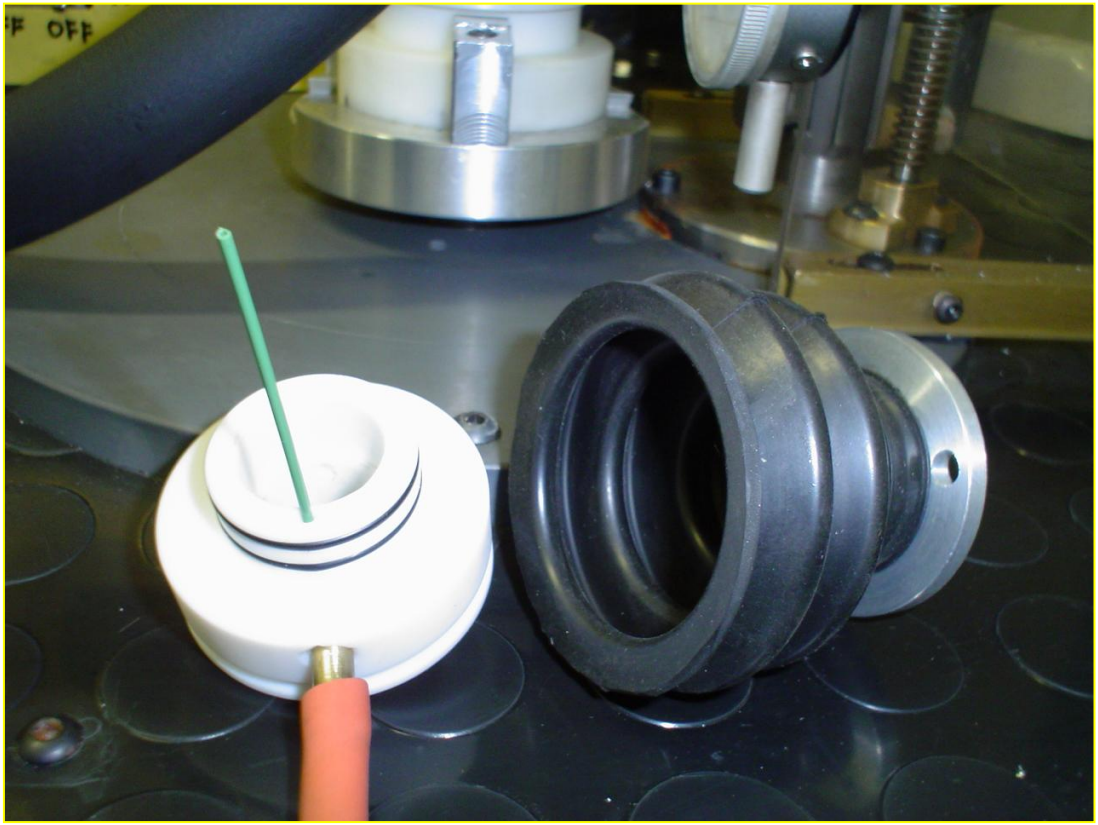


FLOW MULTIHORN SYSTEMS





US UNDER MODIFIED ATHMOSPHERE



US UNDER PRESSURE

CAVITATION MEASUREMENT

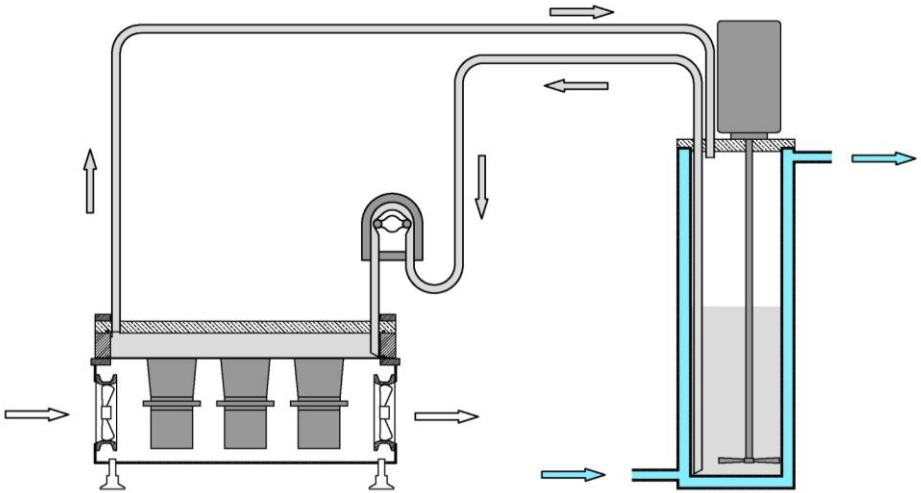
NON-METALLIC CAVITATING TUBE

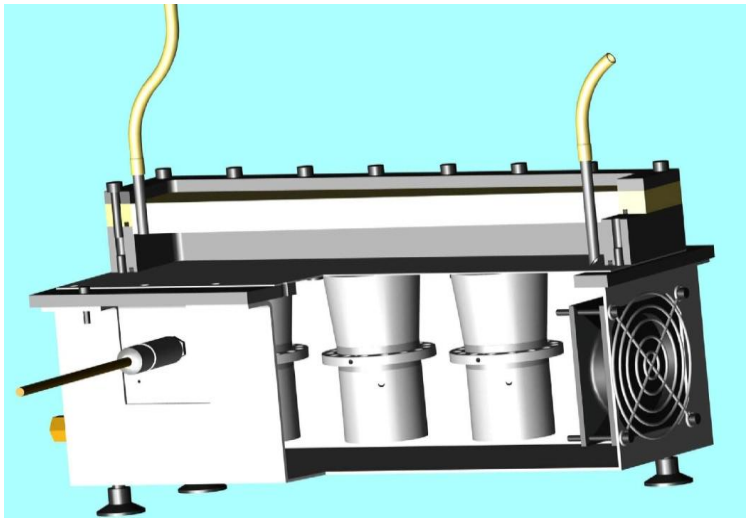
SONICATION IN FLOW MODE

SONIC

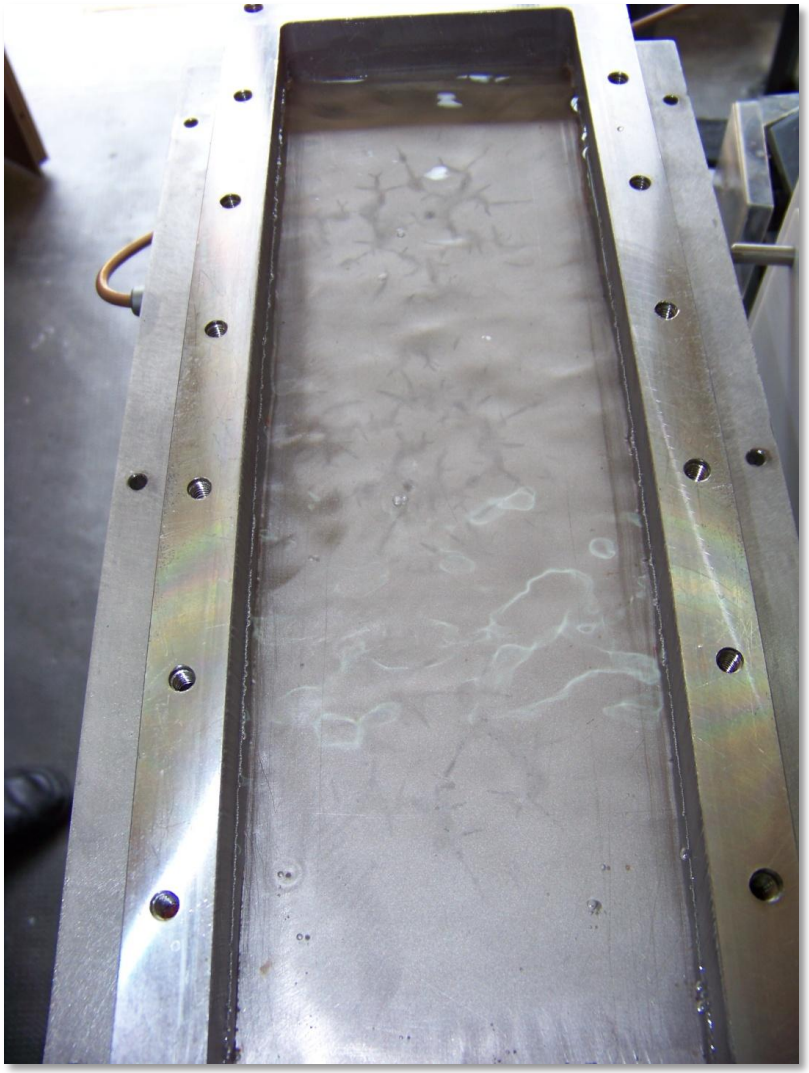
Ultrasound Technology

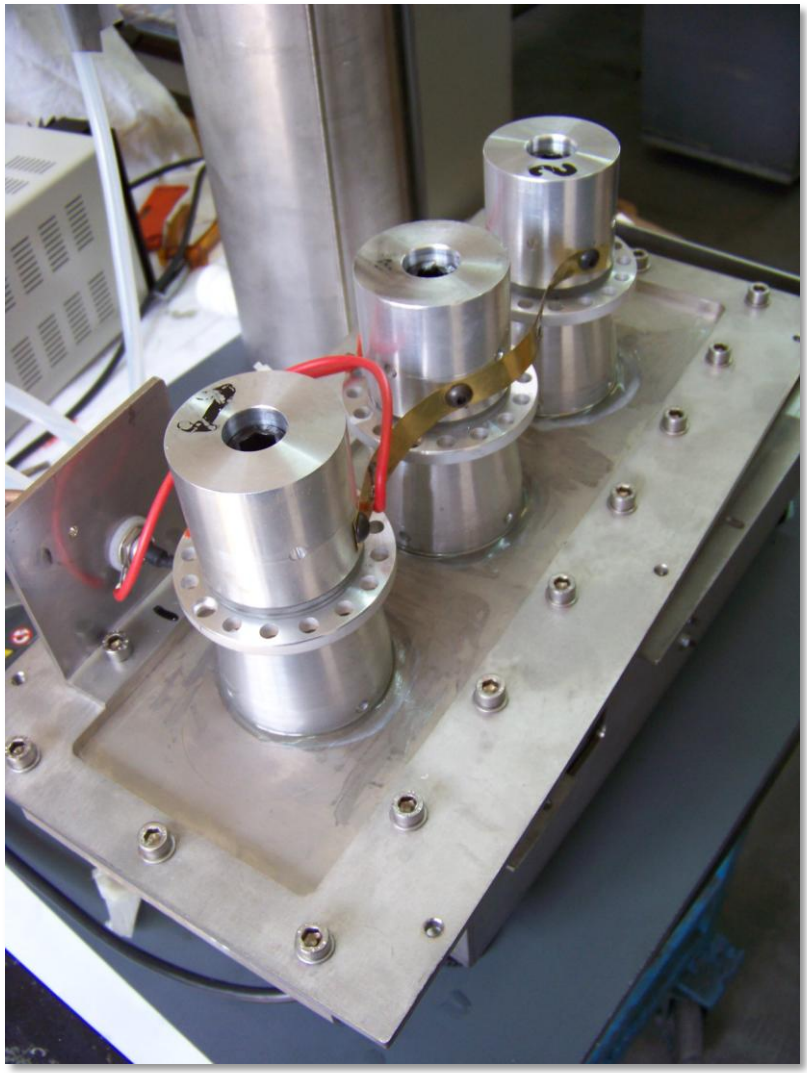
MULTIPROBE FLOW REACTOR



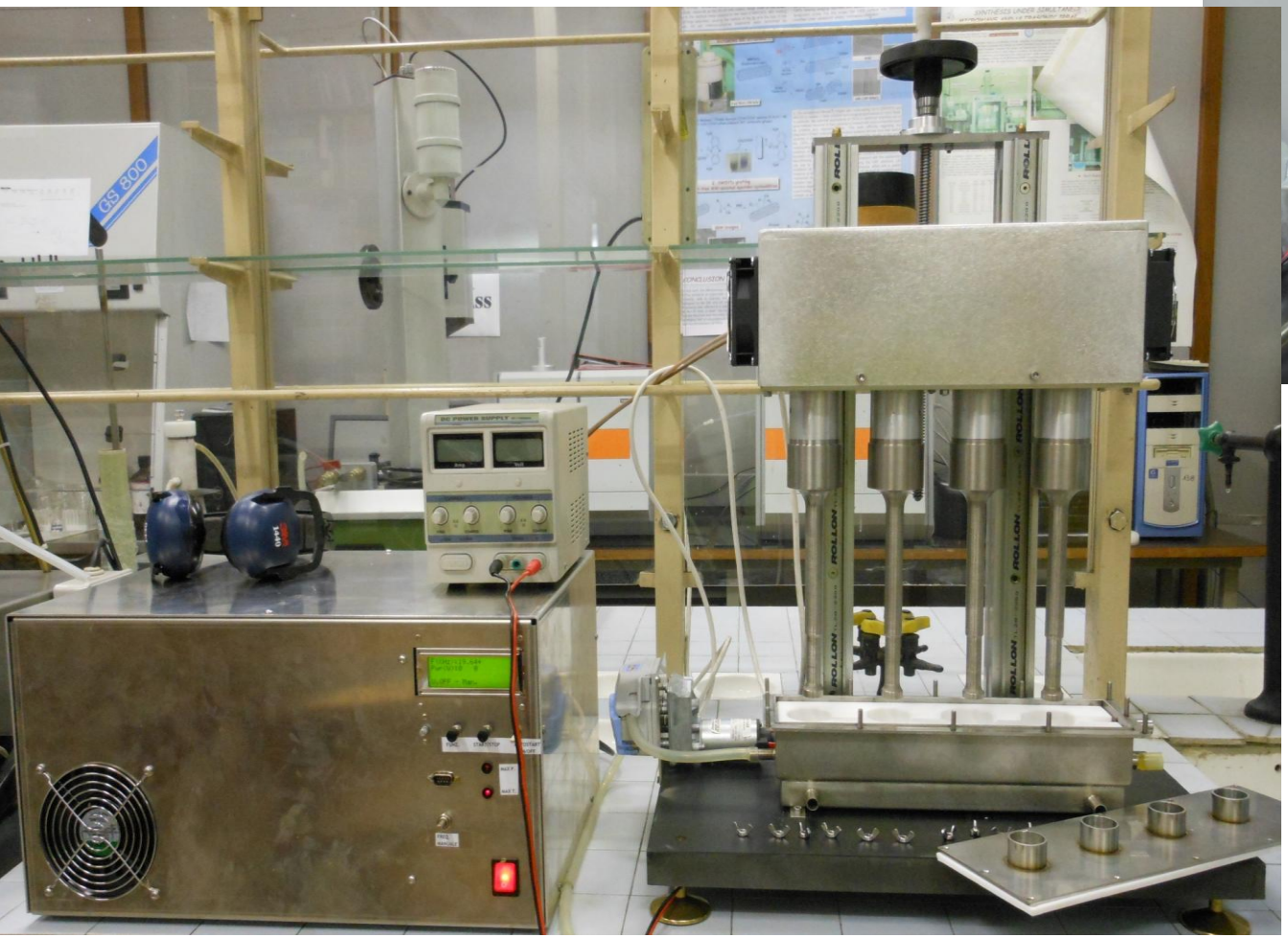


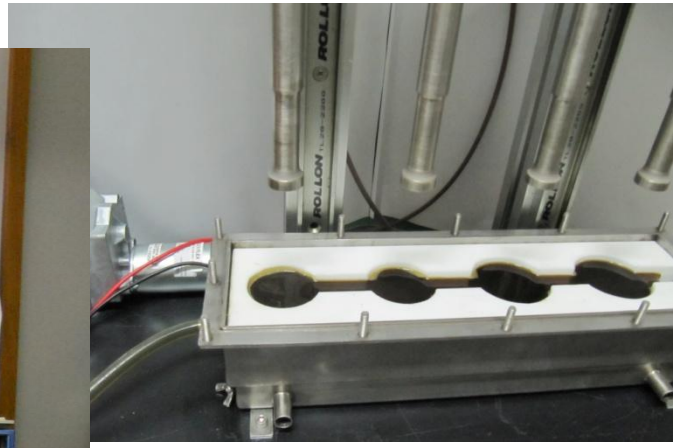
MULTIPROBE FLOW REACTOR

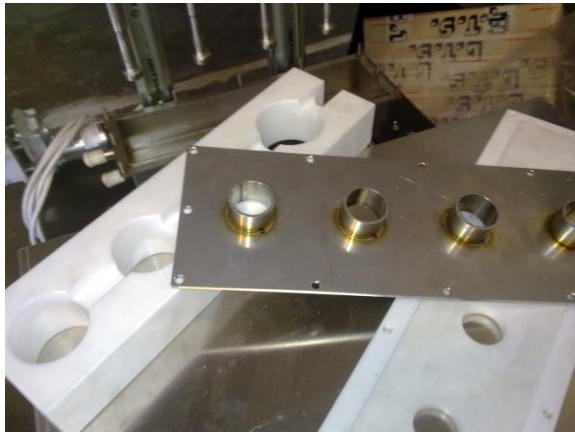




FLOW MULTIHORN SYSTEMS







THANK YOU FOR YOUR ATTENTION!