Block III – Nano-Particles in Ionic Liquids

IoNanofluids – Synthesis, Properties and Applications

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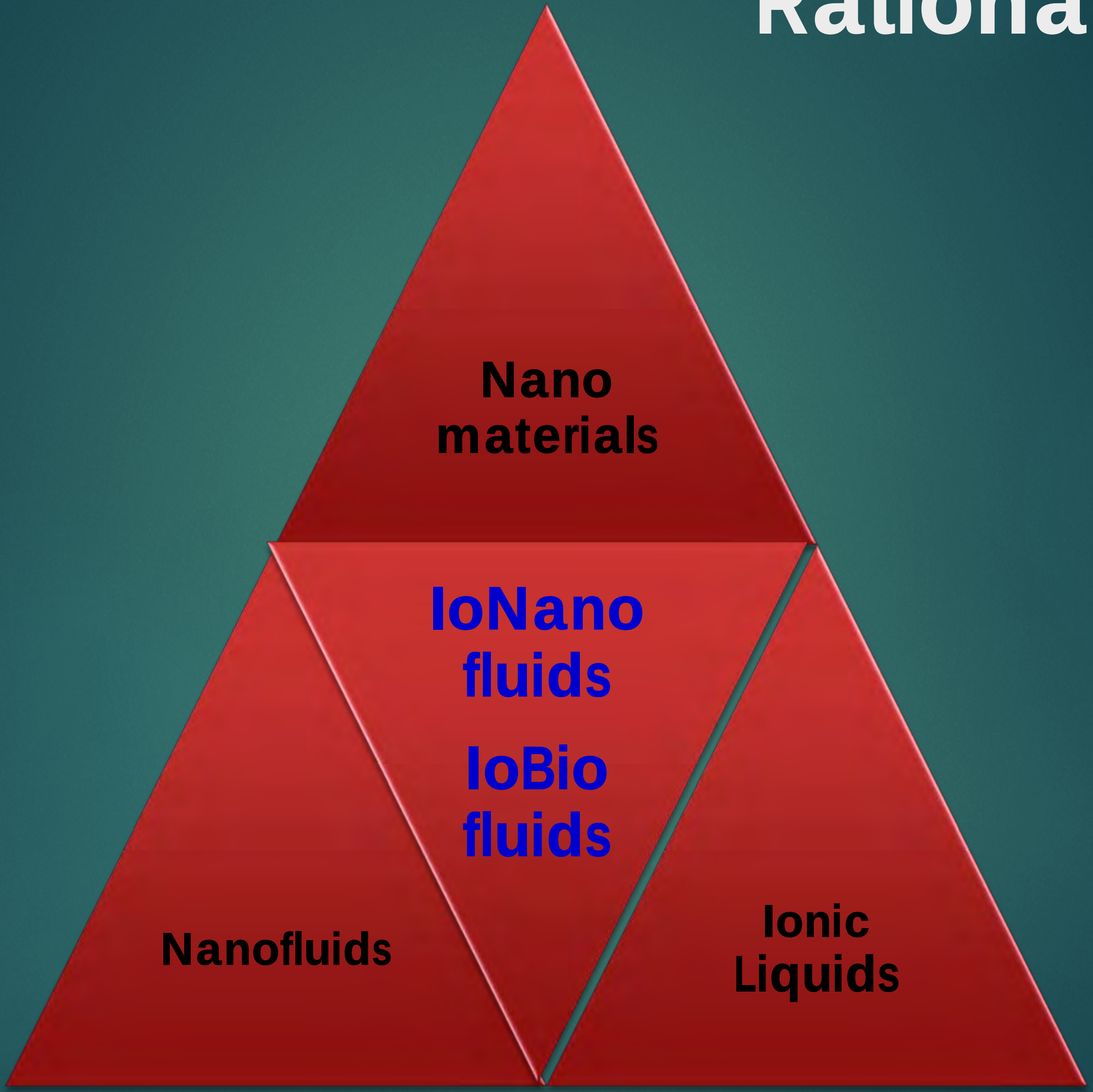
IoNanofluids – Synthesis, Properties and Applications

- What is a IoNanofluid / IoBiofluid?
  - How should it be prepared
  - Nanomaterials
- Results (Experiment, theory)
- Scientific and Industrial Challenges
- Conclusions - Looking Forward
- **Foreseeing Industrial applications**
  - Other process requirements
    - Thermal stability
    - Ecotoxicity of Ionic Liquids, Nanomaterials and IoNanofluids

Rationale


Nano materials
IoNano fluids
IoBio fluids
Nanofluids
Ionic Liquids

Reasons for Studying These Nanosystems

- **Enhanced thermal properties** for heat transfer and heat storage
- Complex interactions create nano-regions that enhance reactivity and **selectivity** of chemical reactions (nanocatalysis)
- IoNanofluids are designable and fine-tunable through base ILs to meet any **specific** application or task requirement
- Non-flammable and non-volatile at ambient conditions, **environmentally** friendly solvents, and reaction fluids
- Really "green" solvents?

Nanomaterials

Nanomaterials

Carbon nanotubes
Fullerene
Graphene
Nanoparticles of elements
Nanoparticles of binary compounds
Nanoparticles of complex compounds
Quantum dots
Nanowires
Nanofibers
Non-carbon nanotubes

Functions

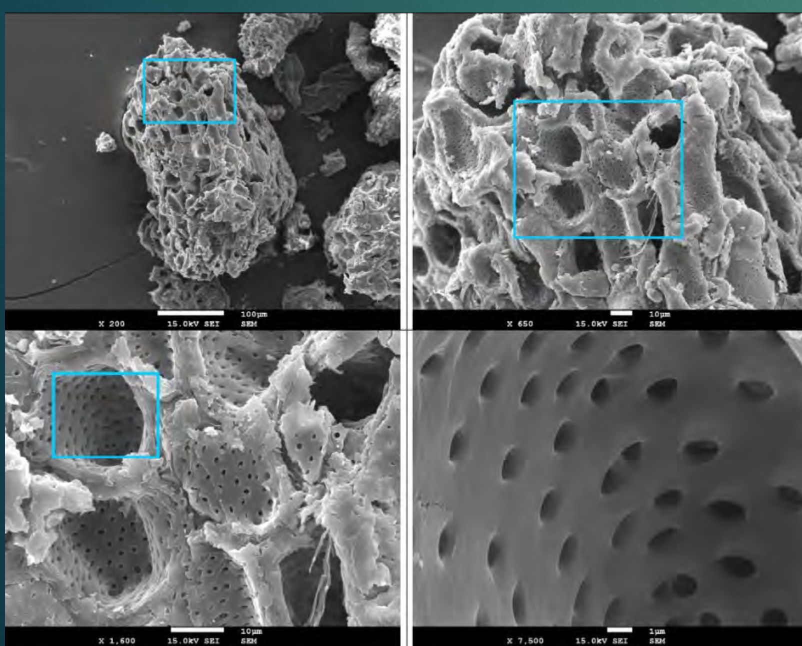
Antimicrobial
Catalyst
Pigment / Coatings
Cosmetic
Environmental treatment
Filtration
Green chemistry
Hardness / strength
Health
Hydrophobic treatment
Lubricant
Miniaturization
Sorbent
Sun protection

Applications

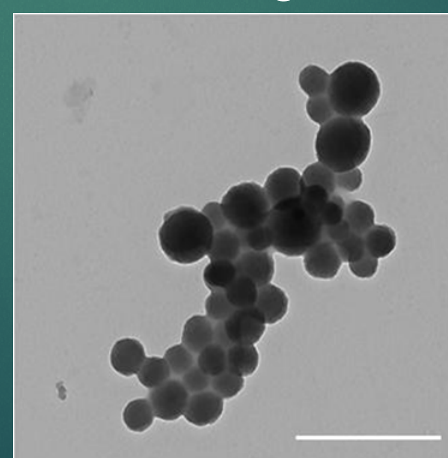
Chemicals
Commodities
Construction
Energy
Environment
Food
Industrial
Information and Communications Technology
Medical
Precision Engineering
Textiles and Garments
Transportation

And More…

- We are in the Nanomaterials World:
  - Nanoparticles (TiO_2, Ag, …)
  - Nanorods or nanotubes (CNT's)
  - Nanosheets (graphene, graphene oxide, …)
  - Complex nature marine materials, fruit seeds, etc…



FEG-SEM images of fruit residues for different magnifications (C. Queirós, 2010)



TEM of marine cuttlefish residue (S I Vieira, 2012)

From Normal Fluids to IoNanofluids

Normal fluids such water, organic solvents, heat transfer oils, lubricants, refrigerants were developed in a wealthy and growing economy

Nanofluids dispersion of nanometer particles, rods or tubes in traditional heat transfer fluids such as water, ethylene glycol, and engine oil - Steve Choi (ANL, USA,1995)

IoNanofluids

Our group 2009: stable dispersion of nanometer particles, rods or tubes in Ionic Liquids $C_n$mim][NTf_2], [C_6mim][BF_4], [C_6mim][DCA], etc.

IoBiofluids – Using nanomaterials from nature

Nanofluid

Nanofluids Preparation Methodology, Chapter 1. in Nanofluids: Synthesis, Properties and Applications (2014)

Enhanced experimental data for thermal conductivity, thermal diffusivity, viscosity and convective heat transfer coefficients compared with the base fluid "oil" or water demonstrated potential applications in many fields.

Nanofluids are not simply mixtures of solids in liquids and its success depends on the method of preparation.

J. Chem. Eng. Data **2010,** *55,* 653–661 **653**

Thermal Properties of Ionic Liquids and IoNanofluids of Imidazolium and Pyrrolidinium Liquids†

C. A. Nieto de Castro,* M. J. V. Lourenço, A. P. C. Ribeiro, E. Langa, and S. I. C. Vieira

Centro de Ciências Moleculares e Materiais and Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

P. Goodrich and C. Hardacre

The QUILL Centre/School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, U.K.

submitted 31/7/2009

Io(nic)Nanofluid

What are your colleagues reading in the *Journal of Chemical & Engineering Data*?

The articles below represent the most read articles from the *Journal of Chemical & Engineering Data* in the full year of 2011. The journal is published monthly and is devoted to the publication of experimental data and the evaluation and prediction of property values.

Journal of chemical & engineering data

Thermal Properties of Ionic Liquids and IoNanofluids of Imidazolium and Pyrrolidinium Liquids

C. A. Nieto de Castro, M. J. V. Lourenço, A. P. C. Ribeiro, E. Langa and S. I. C. Vieira

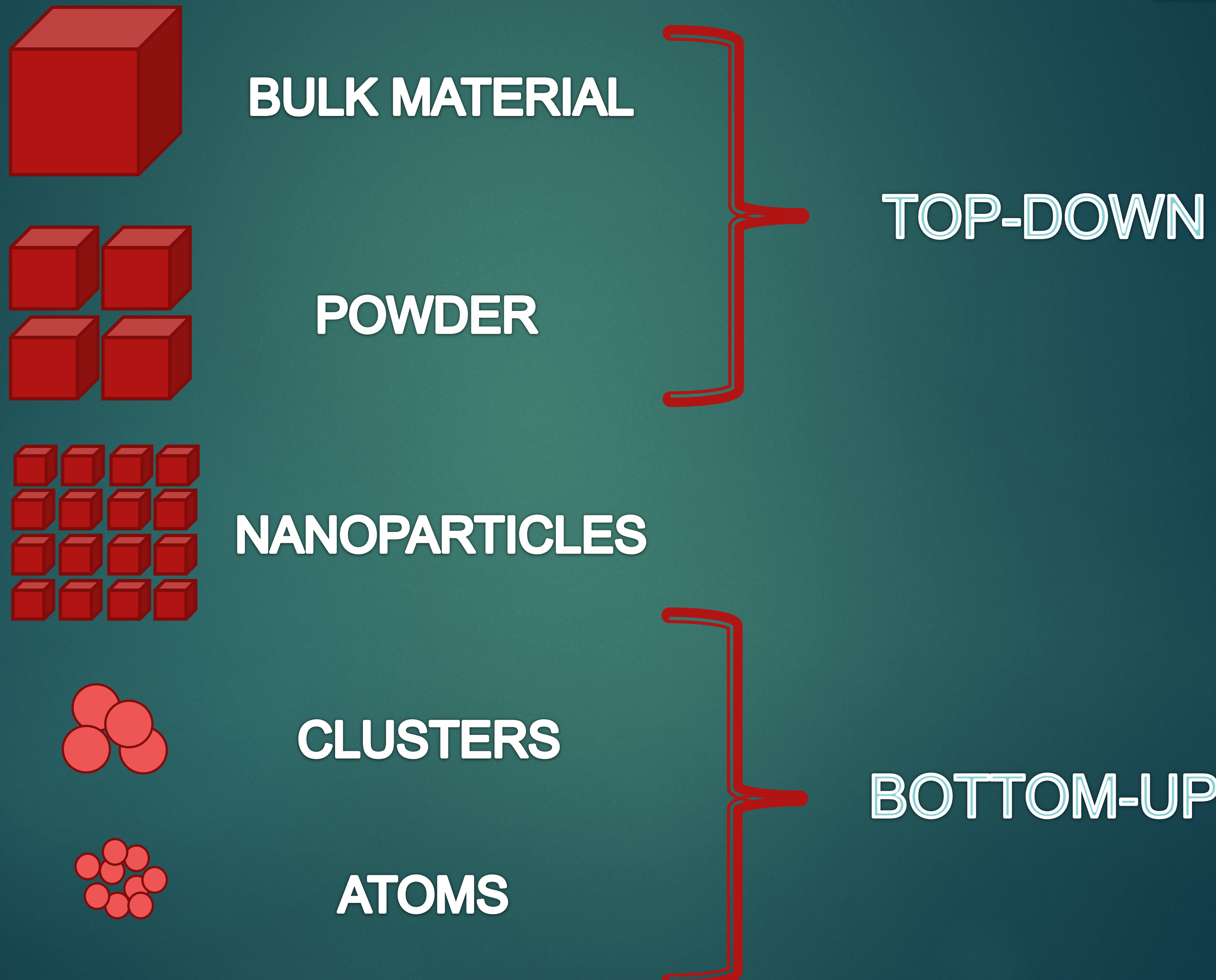
DOI: 10.1021/je900648p

Nanofluid / IoNanofluid / IoBiofluid

Essential requirements: stability over a long period of time, durability of the suspension, prevention of agglomeration and the constancy of the fluid chemistry.

Existing experimental data in the literature **doesn't report**: the characterization of the nanoparticle morphology, temporal behaviour of the suspension, eventual existence of reactivity or physical interaction nanomaterial-fluid, integrity of the nanoparticle in the fluid base, being very reserved with the methods used in the preparation of the nanofluid and how stability was evaluated (?).

Nanomaterial preparation: Bottom-Up and Top-Down Approaches



Nanomaterial preparation: Bottom-Up and Top-Down Approaches

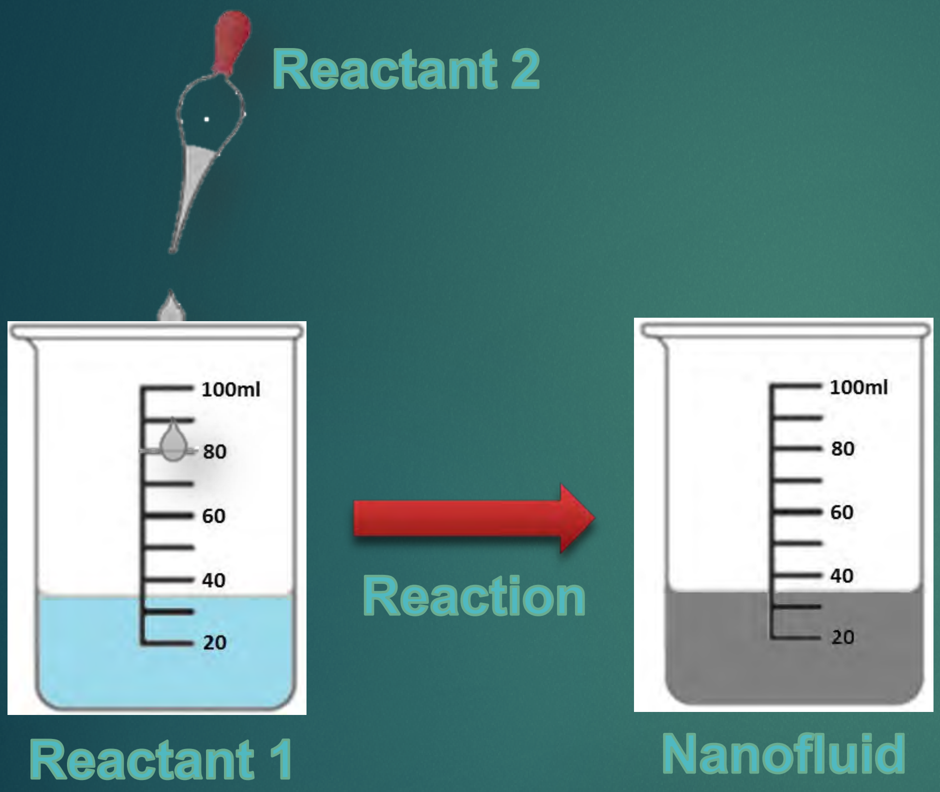
TOP-DOWN

- Attrition
- Milling
- Lithography – etching

BOTTOM-UP

- Colloidal dispersion
- Lithography - growth of thin films
- Nanolithography
- Nano-manipulation

Nanofluid preparation: One Step Method

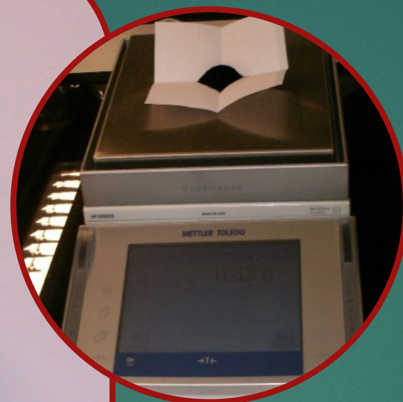


ONE STEP METHOD

- Synthesis of nanofluids in one-step;
- Nanoparticles synthesized in base fluid;
- Reaction: microwave irradiation, ultrasonic agitation, heating, reduction, etc.

Nanofluid preparation: Two Step Method

Nanofluid



TWO STEP METHOD

- Commercial nanomaterial + base fluid;
- Mixing/dispersion: intense agitation, magnetic force, ultrasonic agitation or high pressure homogenization, etc.

Two Step Method vs One Step Method

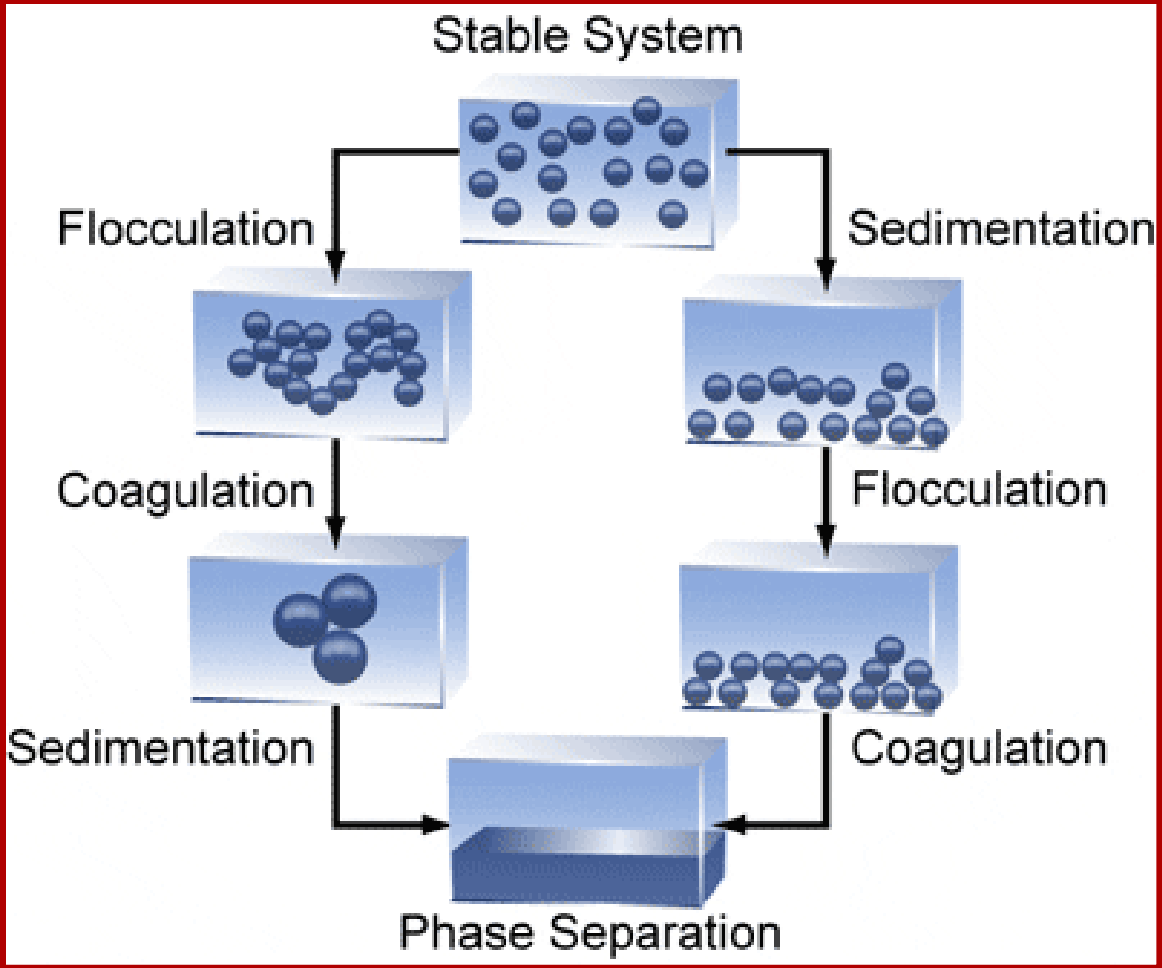
TWO STEP METHOD

- **Advantages**: practical and economic process.
- **Disadvantages**: stability (powders aggregate due to strong van der Walls forces). Internal stress, surface defects, contaminations
- May require surfactants.

ONE STEP METHOD

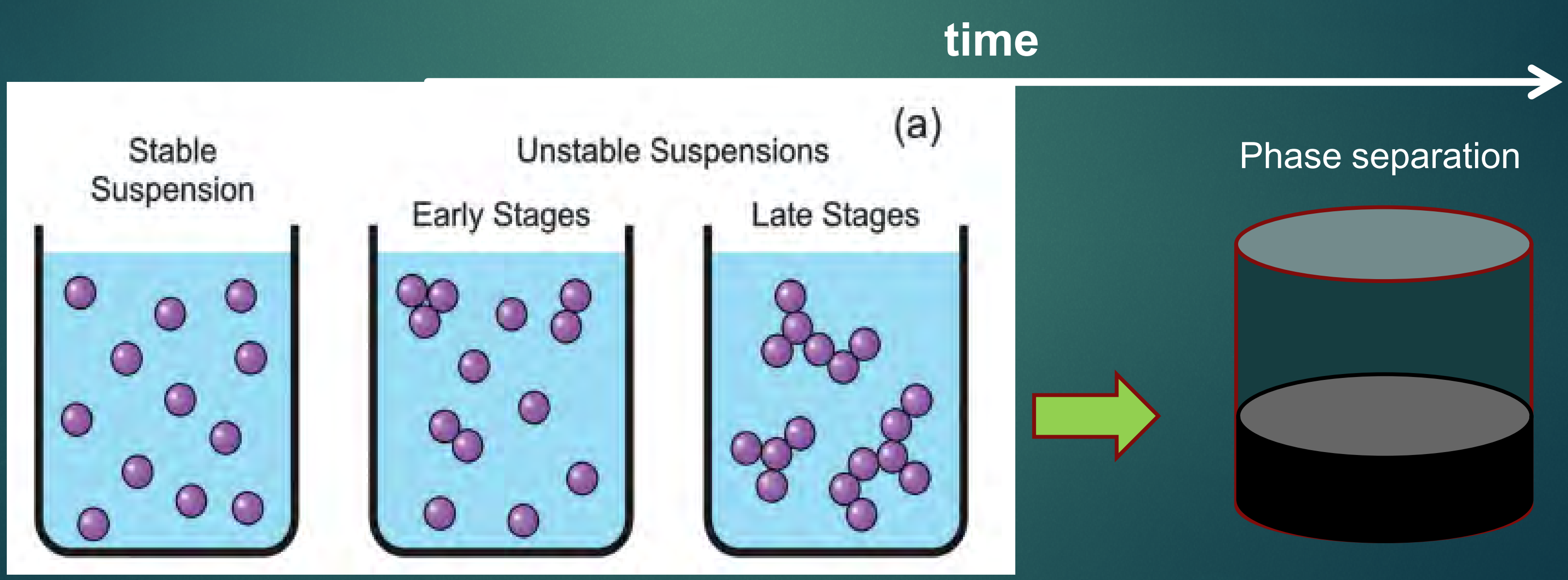
- **Advantages**: nanoparticle agglomeration minimized (transportation, storage, drying and dispersion of nanoparticles is avoided).
- **Disadvantages**: use of low vapour pressure fluids.

Nanofluids stability



Particle Aggregation

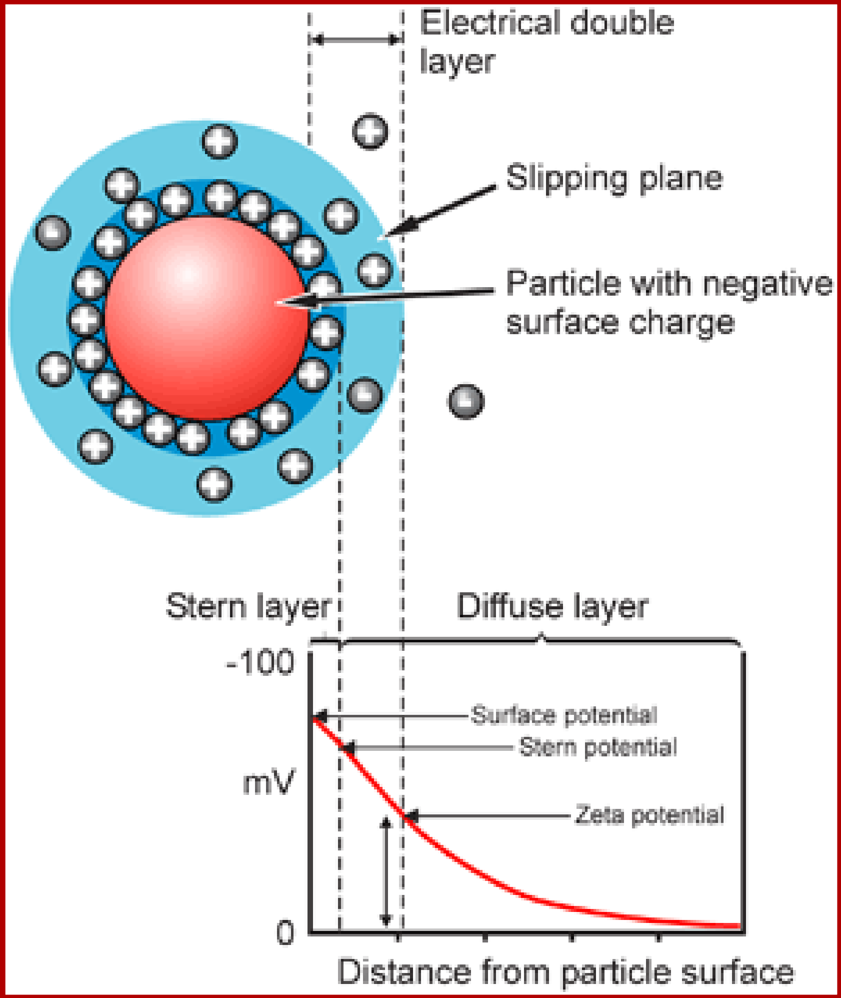
- Aggregation of NP's in ionic liquids is caused by a competition between WDW (or polar) forces and double layer forces screening caused by ions, at the particle/IL interface
- **VDW forces are attractive and DL forces are repulsive**
- Balance between these forces control aggregation of NP's in IL's, and therefore the stability of a dispersion in the IoNanofluid.



Istvan Szilagyi, Adapted from PCCP, 16, 9515, (2014)

Nanofluids stability Methods

Nanofluid stability: zeta potential



Zeta Potential: stabilization

Zeta Potential: coagulation or floculation

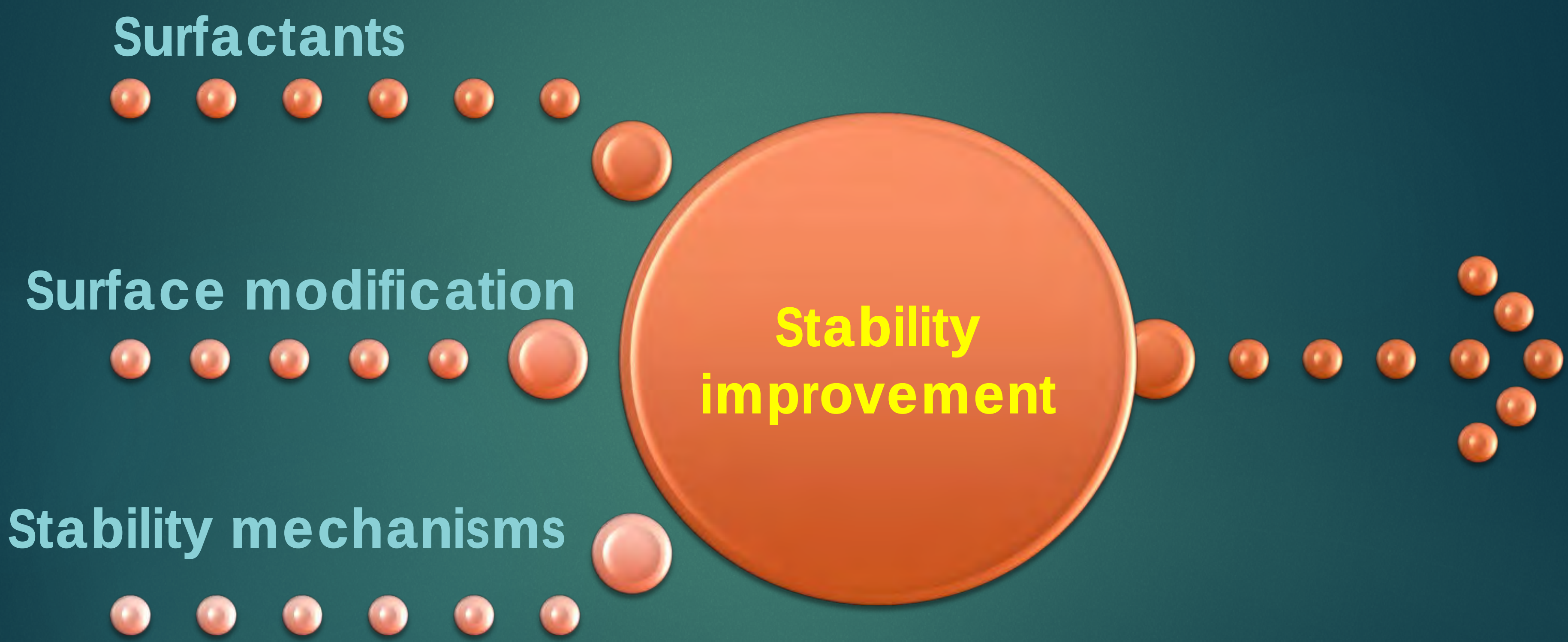
Very stable

|40| - |60| mV

Excellent stability

|60| mV

Nanofluids stability



Nanofluid preparation by ultrasonic energy method

METHOD

- Efficient, precise, fast, with less contamination;
- Can result in efficient suspensions/chemical reactions, but if done incorrectly, can end in larger agglomerates.

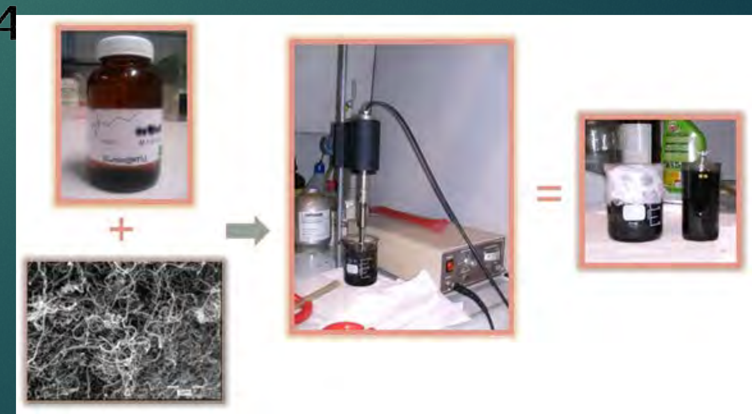
SONICATION PARAMETERS

- Temperature
- Time, frequency and operation mode
- Sample volume and concentration
- Probe and vessel
- Aerosoling and foaming
- Solvent characteristics

Nanofluid preparation by ultrasonic energy method

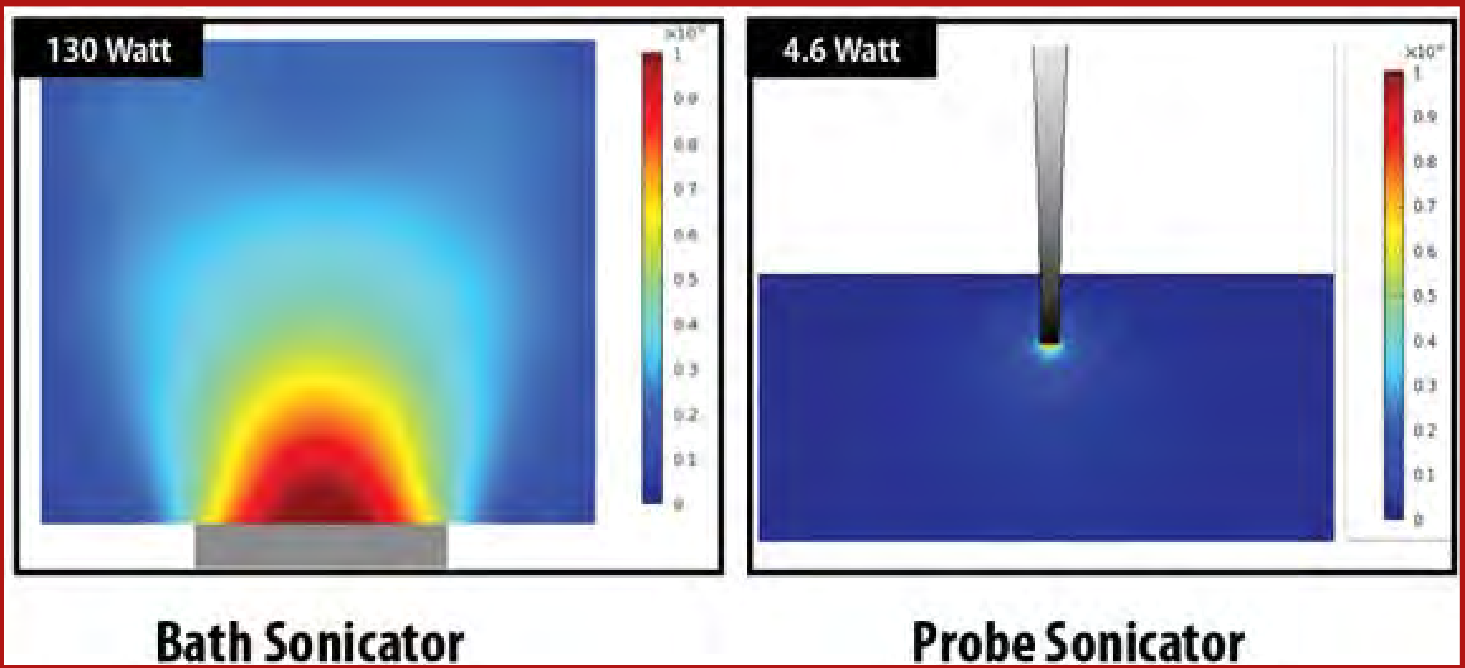
hielscher
Ultrasound Technology

carbon_nanotubes_2_p0640x0360.mp4



Optimizing sonication

- **Direct sonication (probe)**: recommended, energy output received by the materials is higher.
- **Ultrasonic bath**: operates at lower energy levels, suggested for re-suspensions of samples that were previously sonicated directly or when higher energy levels can cause unintentional alterations or damages to the particles



Optimizing sonication

Trial and error

1st: see if a stable dispersion is possible,

High power output

Low sample volume,

High solid Concentration

Prolonged sonication time

2nd: measure medium size distribution particle – DLS of nanofluid

3rd: select time, concentration and volume

Vary power output

Determine best value of energy supply

Best methodology

What is the nanofluid target?

Fluid and nanomaterial selection

Which suppliers?

FLUID: purity, characterization, physico-chemical properties, timelife expectancy	NANOMATERIAL: purity, characterization geometry, dimensions, identity insurance

Which preparation method? Suitability

ultrasound probe	ultrasound bath

Time and temp. control - avoid evaporation, protect people from ultrasound noise

immersion, damage/corrosion probe, compatibility of the vessel/shape material	frequency level, bath fluid

Nanofluid stabilization guaranty

depending on the target, evaluate the time of stabilization

Nanofluid characterization: properties measurements, nanomaterial envolded

nanofluid toxicity parameters and waste best environmental disposable

Most important

- To characterize particle size distribution (PSD) in nanofluid (DLS), not the nanomaterial only
- There is always "free" nanoparticles and clusters of n-particles, especially if the distribution has a large width

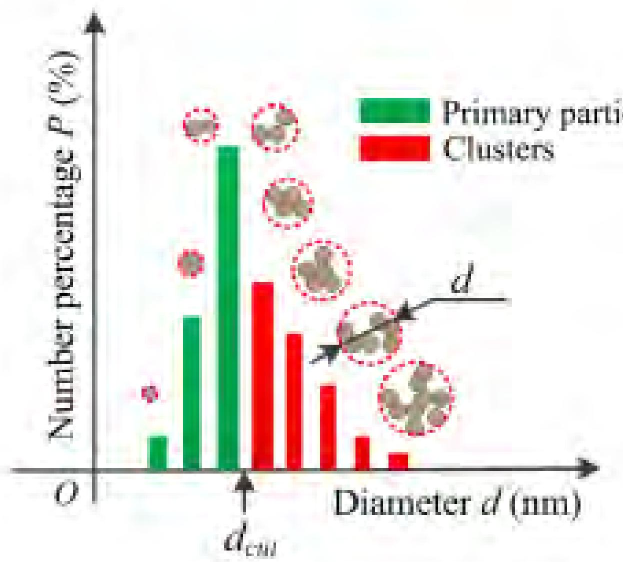


FIG. 2. Schematic of particle size distribution of nanofluids. $2d_{sp}$ is adopted as the cut-off diameter d_{cut} to distinguish between "clusters" and "primary particles" in present model.

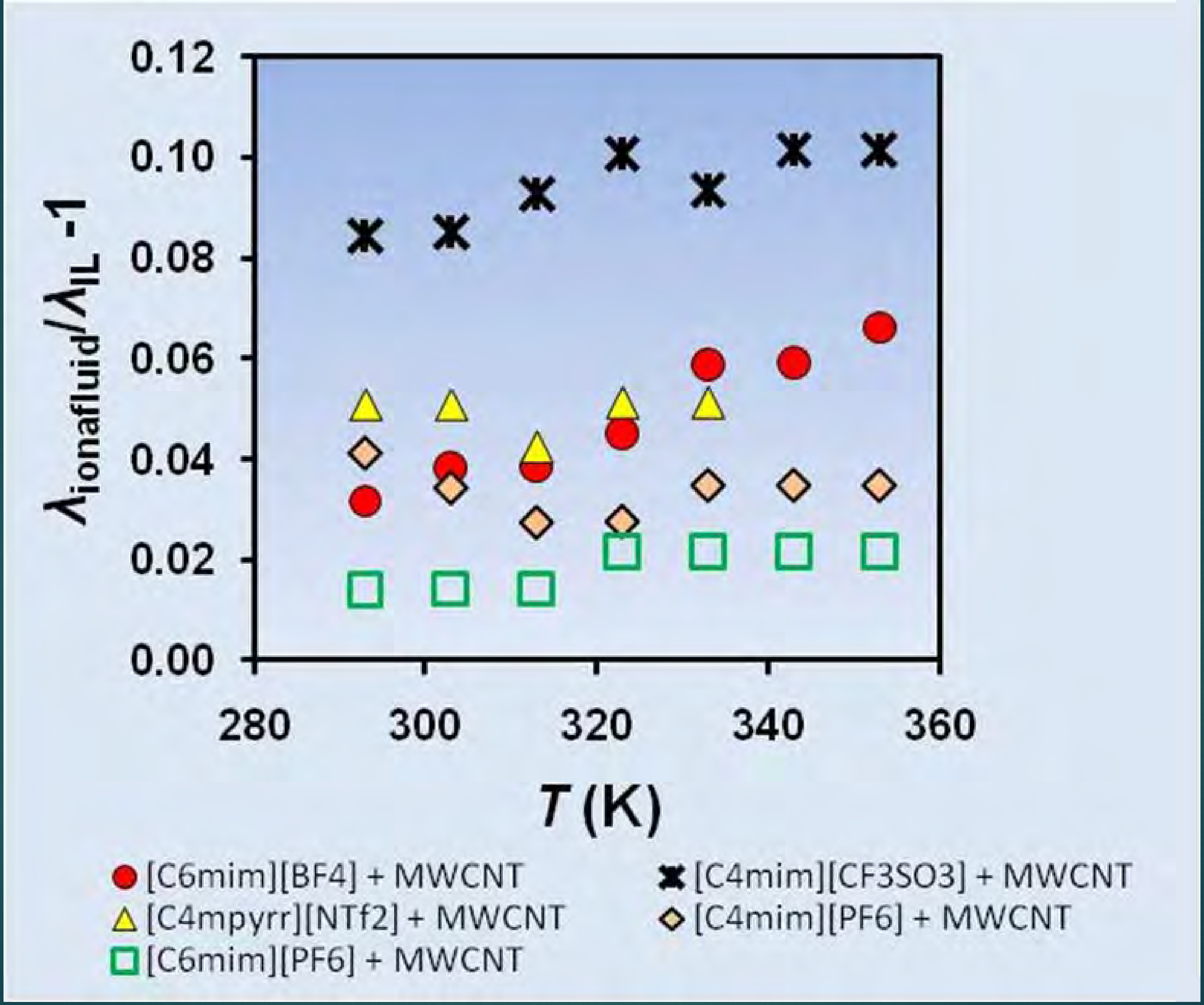
Dengquing Zhou, Huiying Wu, Appl. Phys. Letters, **105**, 083117 (2014)

Properties

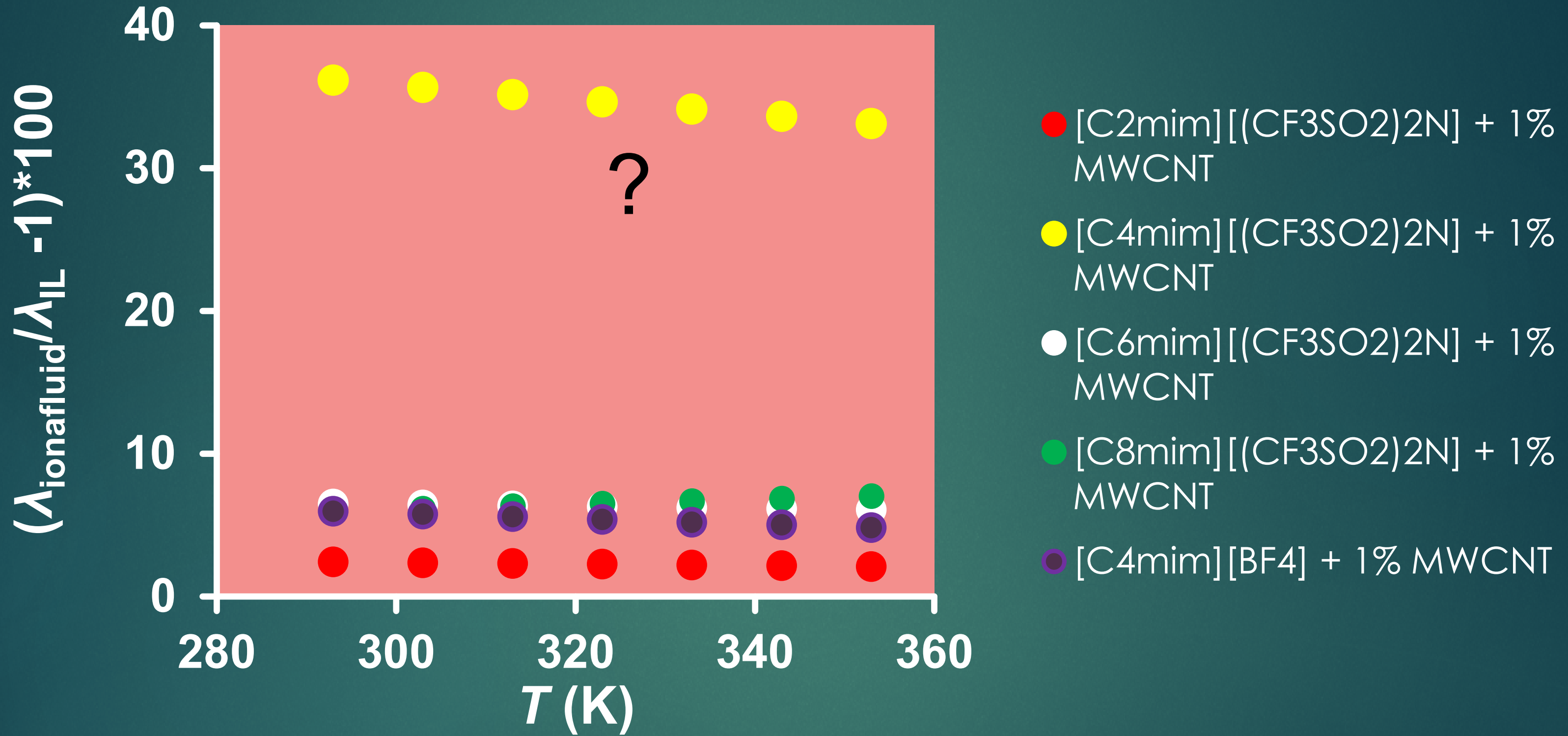
THERMAL CONDUCTIVITY ENHANCEMENT

FOR DIFFERENT IONANOFLUIDS

The first ones ....



n-alkyl-methyl-imidazolium with NTf_2



A P C Ribeiro, S I C Vieira, P Goodrich, C Hardacre, M J V Lourenço, C A Nieto de Castro, *"Thermal conductivity of [Cnmim][(CF3SO2)2N] and [C4mim][BF4] IoNanofluids with carbon nanotubes – Measurement, theory and structural characterization"*,

J. Nanofluids 2, 55–62 (2013)

CNT Nanofluids Preparation

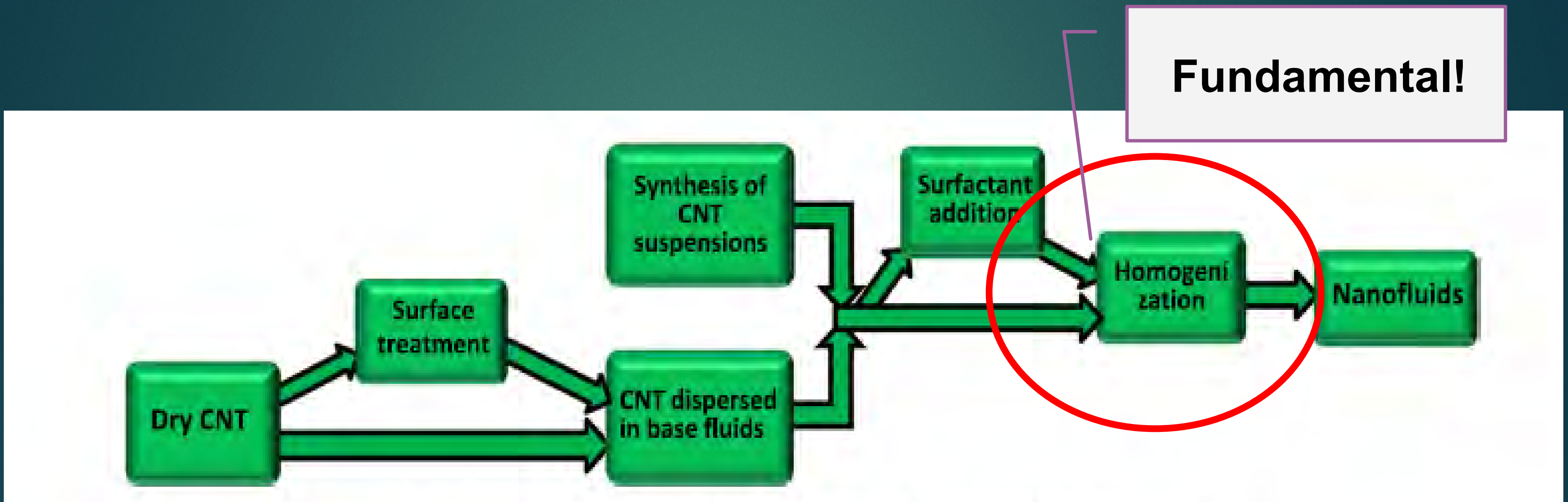
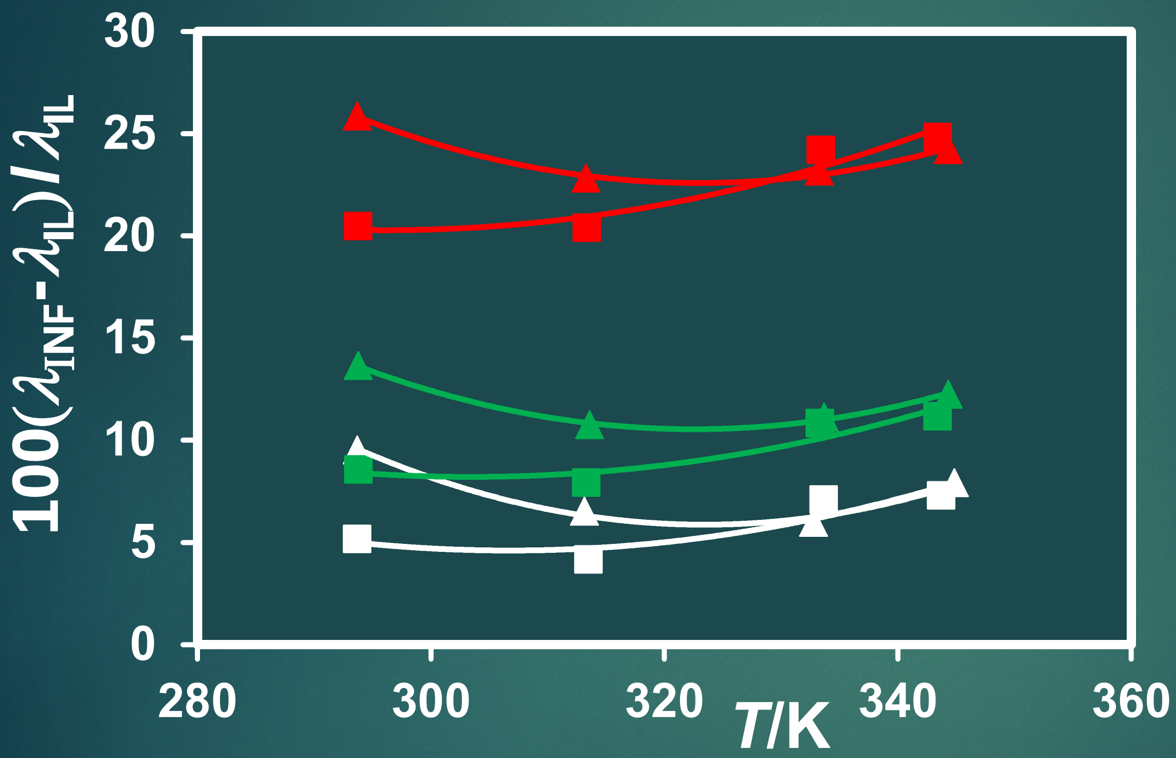


Fig. 3. Flow diagram of CNT-nanofluids preparation processes.

S M Sohel Murshed and C A Nieto de Castro,
"Superior Thermal Features of Carbon Nanotubes Based Nanofluids- A review"
Renewable and Sustainable Energy Reviews, 37, 155–167, 2014

M J Lourenço and S I Vieira,
"Nanofluids Preparation Methodology", Chapter 1 in Nanofluids: Synthesis, Properties and Applications"
S M Sohel Murshed and C A Nieto de Castro, Eds., **NOVA Science Publishers, Inc., New York, 2014**

Thermal Conductivity Enhancement



$[C_4mim][(CF_3SO_2)_2N]$ – squares

$[C_2mim][EtOSO_3]$ – triangles

▲, ■- 0.5% w/w MWCNT's

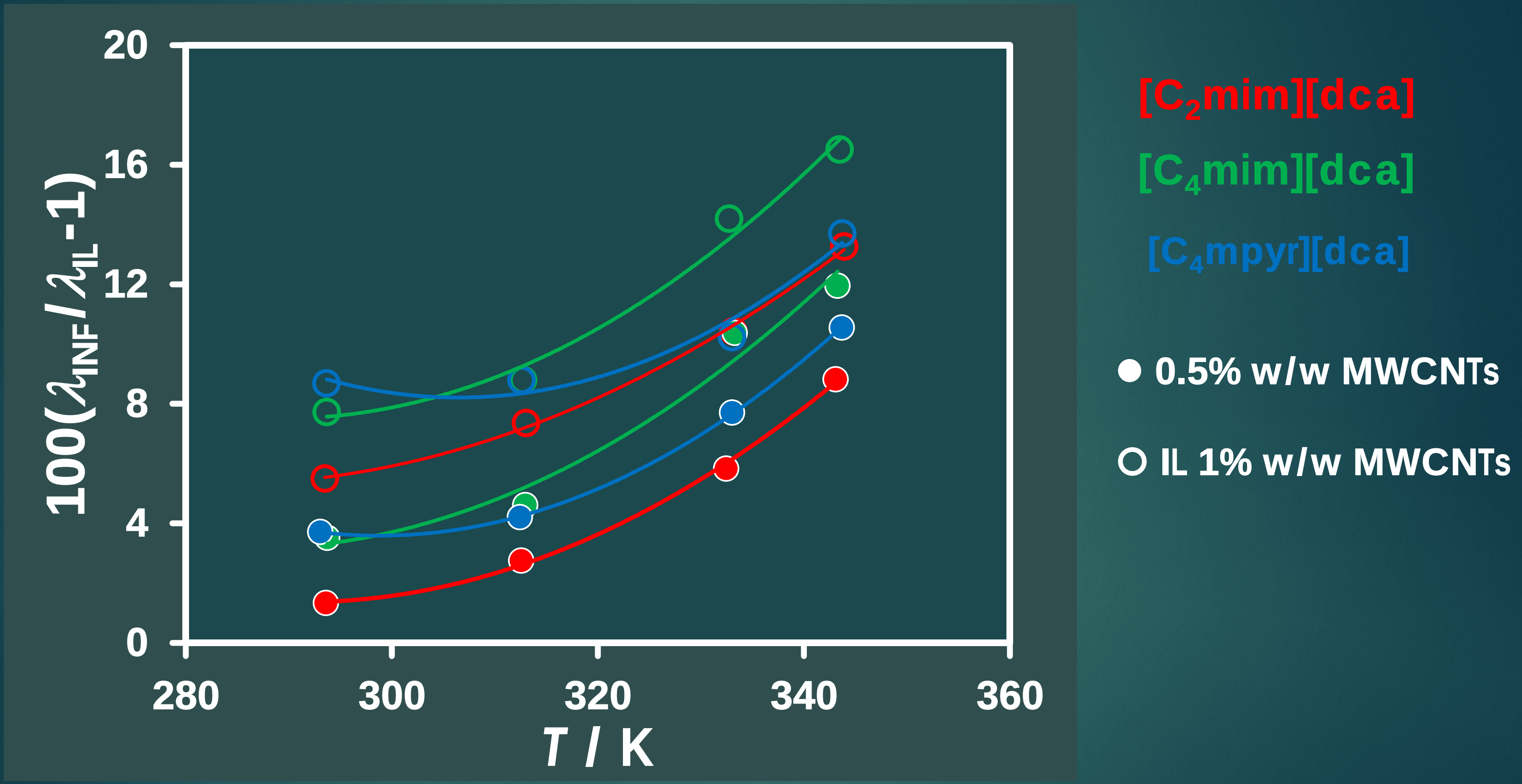
▲, ■ - 1% w/w MWCNT's

▲, ■- 3% w/w MWCNT's

J M P França, S I C Vieira, M J V Lourenço, S M S Murshed, C A Nieto de Castro, *"Thermal Conductivity of $[C_4mim][(CF_3SO_2)_2N]$ and $[C_2mim][EtSO_4]$ and their IoNanofluids with Carbon Nanotubes: Experiment and Theory"*

J. Chem Eng. Data, 58, 467−476, 2013

Dicyanamide fluids

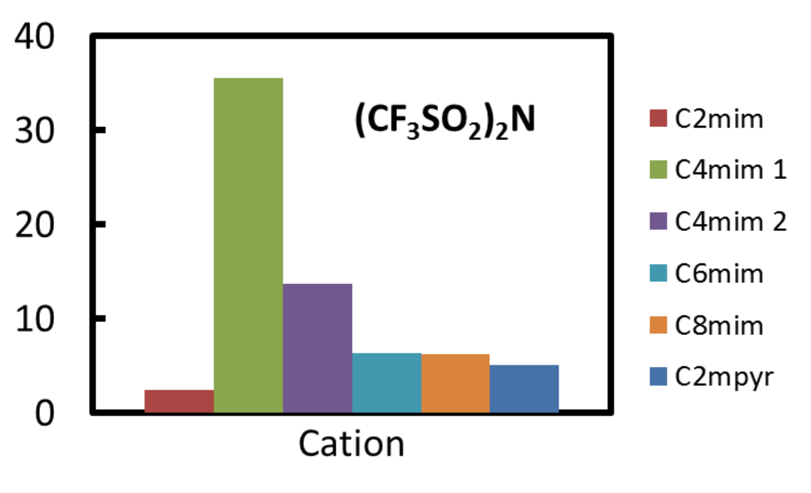


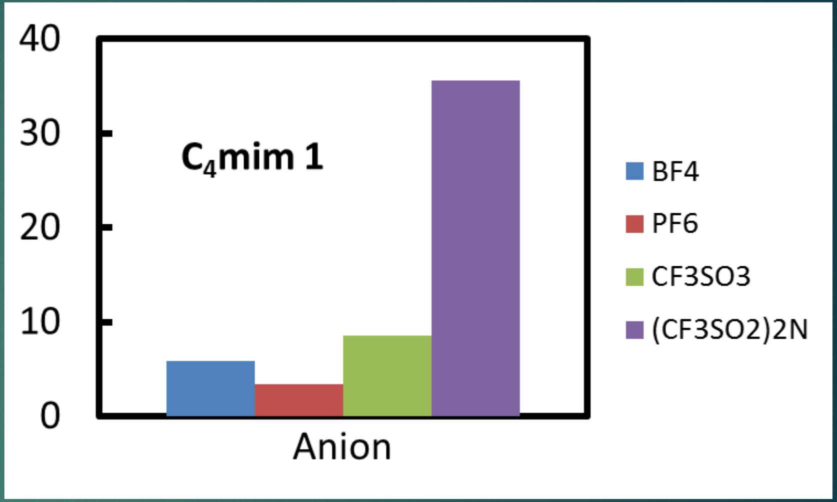
J M P França, S I C Vieira, S M Sohel Murshed, M J V Lourenço, C A Nieto de Castro, A A Pádua
"Thermophysical Properties of Ionic Liquid Dicyanamide (DCA) Nanosystems",
J. Chem. Thermodyn. 2014, , 79 (2014) 248–257

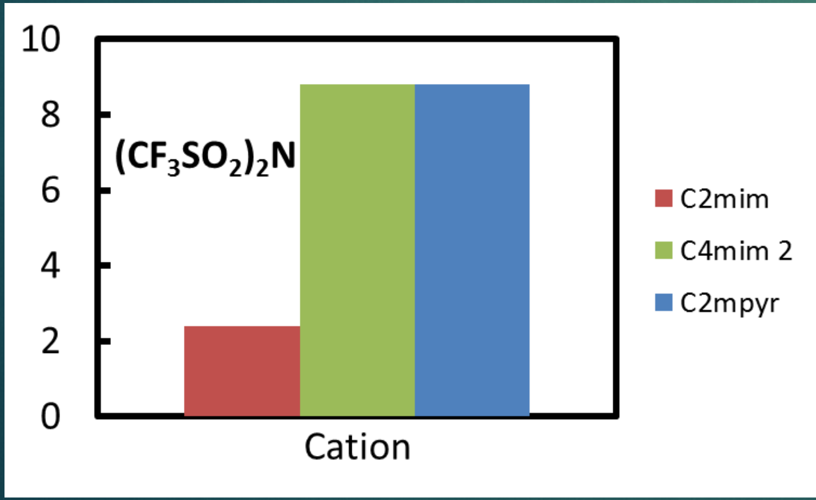
Results Summary, 303 K, 1% MWCNT

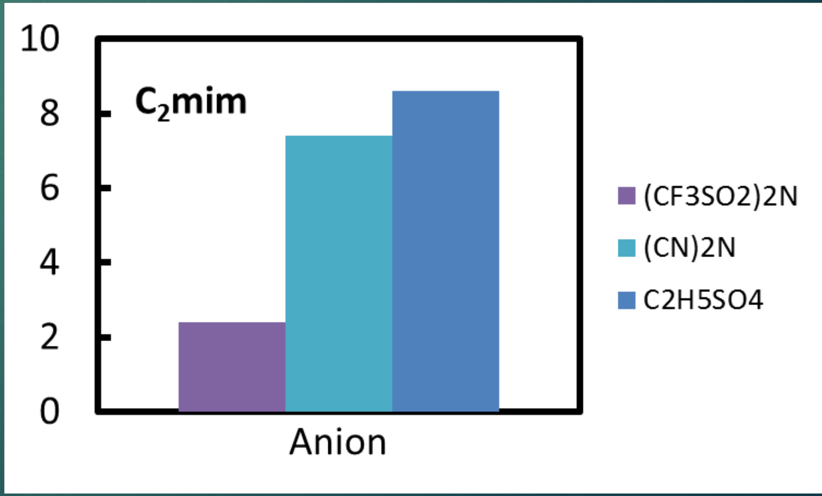
	BF_4	PF_6	CF_3SO_3	$(CF_3SO_2)_2N$	$C_2H_5OSO_3$ ECOGEN	$(CN)_2N$
C_2mim	-	-	-	2.4	8.6	7.4
C_4mim	5.8	3.4	8.5	35.6[1]; 13.7[2]	-	8.8
C_6mim	3.8	1.4	-	6.4	-	-
C_8mim	-	-	-	6.2	-	-
C_2mpyr	-	-	-	5.1	-	8.8

Keeping the same anion or cation







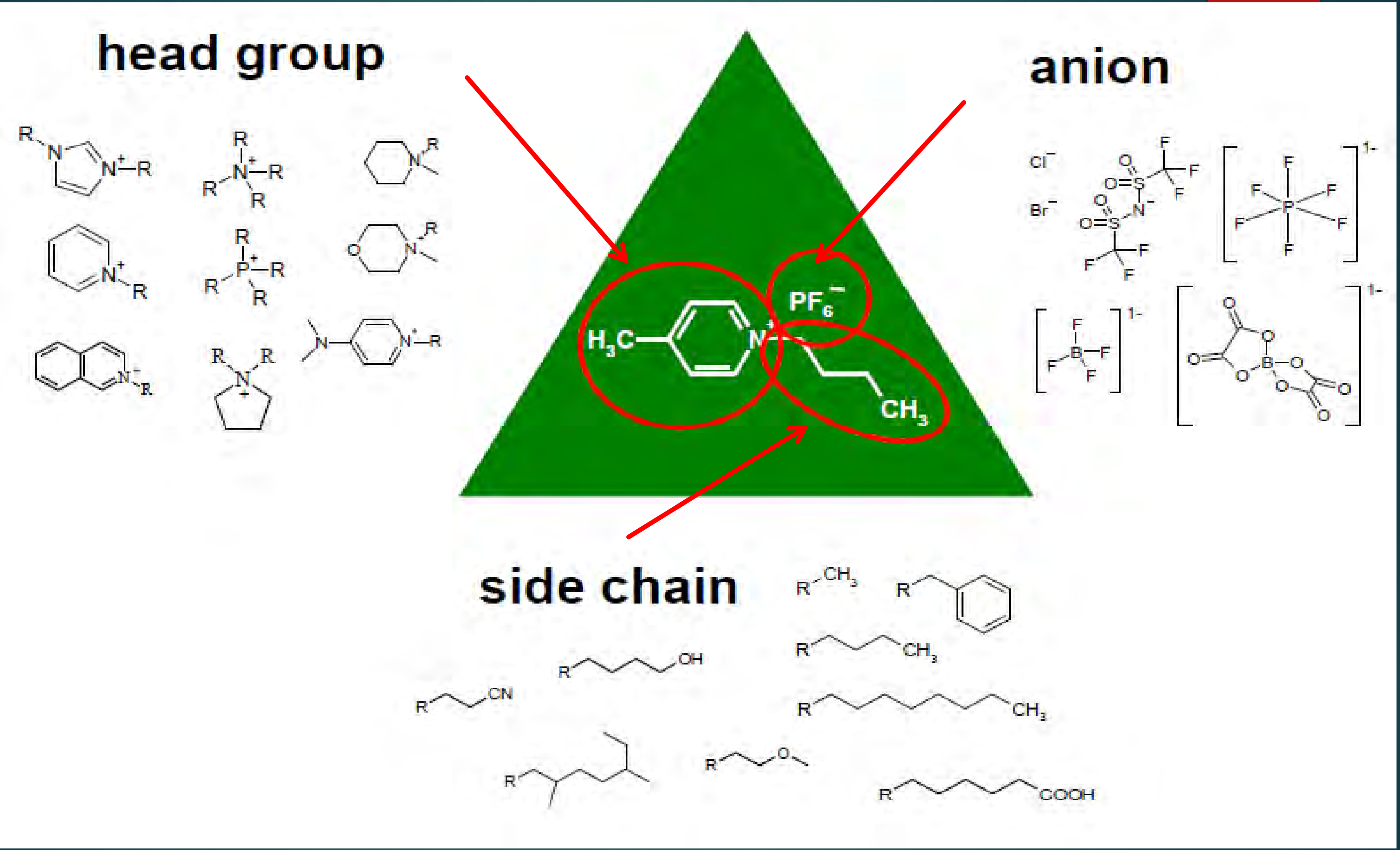


Some Conclusions

- The enhancement is significant for all the fluids studied
- It depends slowly on temperature, except for the DCA liquids
- It depends strongly on the mass/volume fraction
- These results are similar to those obtained when the base fluid is not a IL

Some Molecular Thoughts

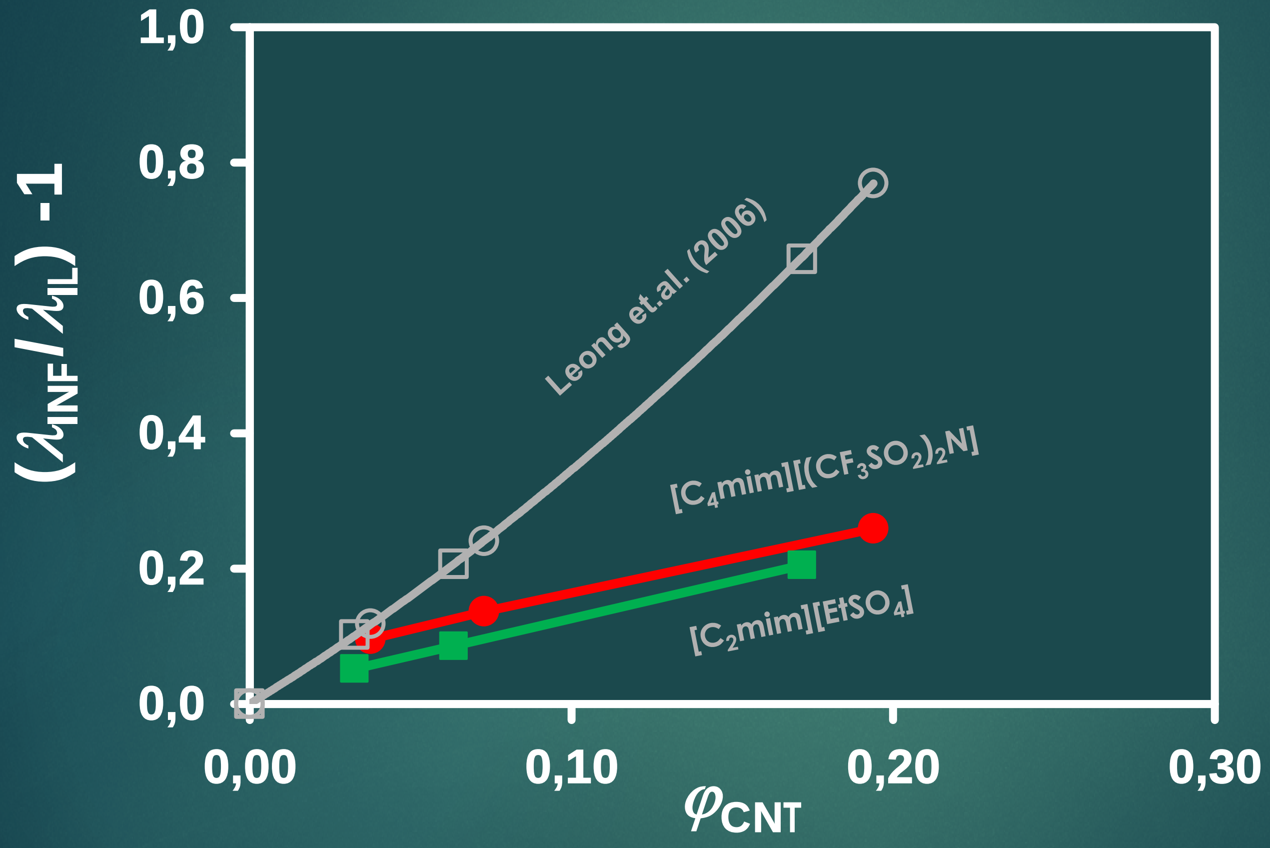
- $[C_4mim][DCA]$ benefits more from the addition of MWCNTs, as the enhancement of the thermal conductivity is higher
  - greater increase in the organization of the liquid nano-structure, favoring a higher transfer of heat
- For the DCA liquids, since the anion is the same and if we take into account the idea of the organization increase when adding MWCNTs, we could infer that **the cation is the controlling factor for the differences in structure of the pure ionic liquids**, and also for the IoNanofluids
- The compounds studied can be separated into **head group** (imidazolium or pyrrolidinium with methyl substitution), an **aliphatic side chain** and an **anion** (the same)



Adapted from Stefan Stolte, Univ Bremen, *"(Eco)Toxicity and Biodegradation of ionic liquids*, REGALIS Summer School, Grove - Pontevedra 9th-12nd JUNE 2013

- Changing the **side chain length**, **the enhancement in the thermal conductivity increases**, possibly due to a better interaction between this chain and the carbon nanotube surface (non-polar entities) that facilitates heat transfer.
- The same effect was found for the [$C_n$mim][$(CF_3SO_2)_2N$] family, ranging from n = 2 to n = 8
- The **change of the head group does not seem to affect the enhancement**, except for volume fraction of the nanotube greater than 0.04, where the methylimidazolium seems to win
- For liquids that have the same cation, [C_2mim], and different anions, [$N(CN)_2$], [$C_2H_5OSO_3$] and [$(CF_3SO_2)_2N$], **the anion structure affects the enhancement**, with the [$(CF_3SO_2)_2N$] salt having the smallest and the [$C_2H_5OSO_3$] the highest. The same result is obtained when we compare the liquids based on the [C_4mim] cation, with the [$(CF_3SO_2)_2N$] salt having smaller enhancement than the [$N(CN)_2$] one

Do existing theories predict this enhancement?



No!

Not sensitive to IL structure

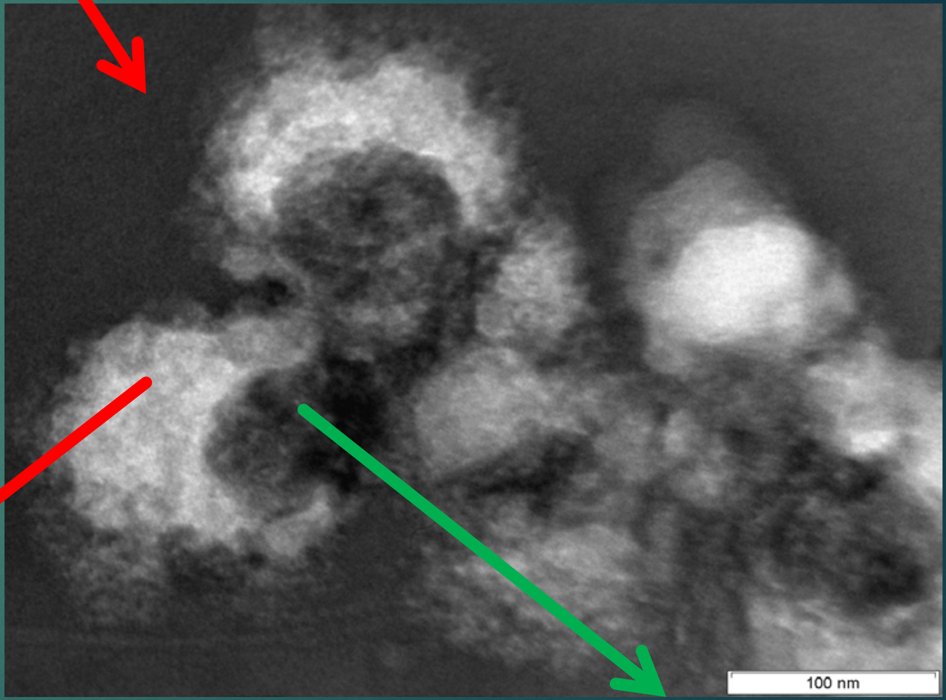
Overestimates value

J M P França, S I C Vieira, M J V Lourenço, S M S Murshed, C A Nieto de Castro, “Thermal Conductivity of $[C_4mim][(CF_3SO_2)_2N]$ and $[C_2mim][EtSO_4]$ and their IoNanofluids with Carbon Nanotubes: Experiment and Theory”, **J. Chem Eng. Data, 58, 467−476, 2013**

Reasons for the enhancement in thermal conductivity?

- There is a big controversy about the heat transfer mechanisms in nanofluids (see our book)
- Some models justify the importance of the interfacial layer between the nanoparticle and the liquid
- First images of IoNanofluids at the nanoscale in our group seem to prove that this is true!

TEM characterization of the $[C_4mim][BF_4]$ + 1% MWCNT IoNanofluid

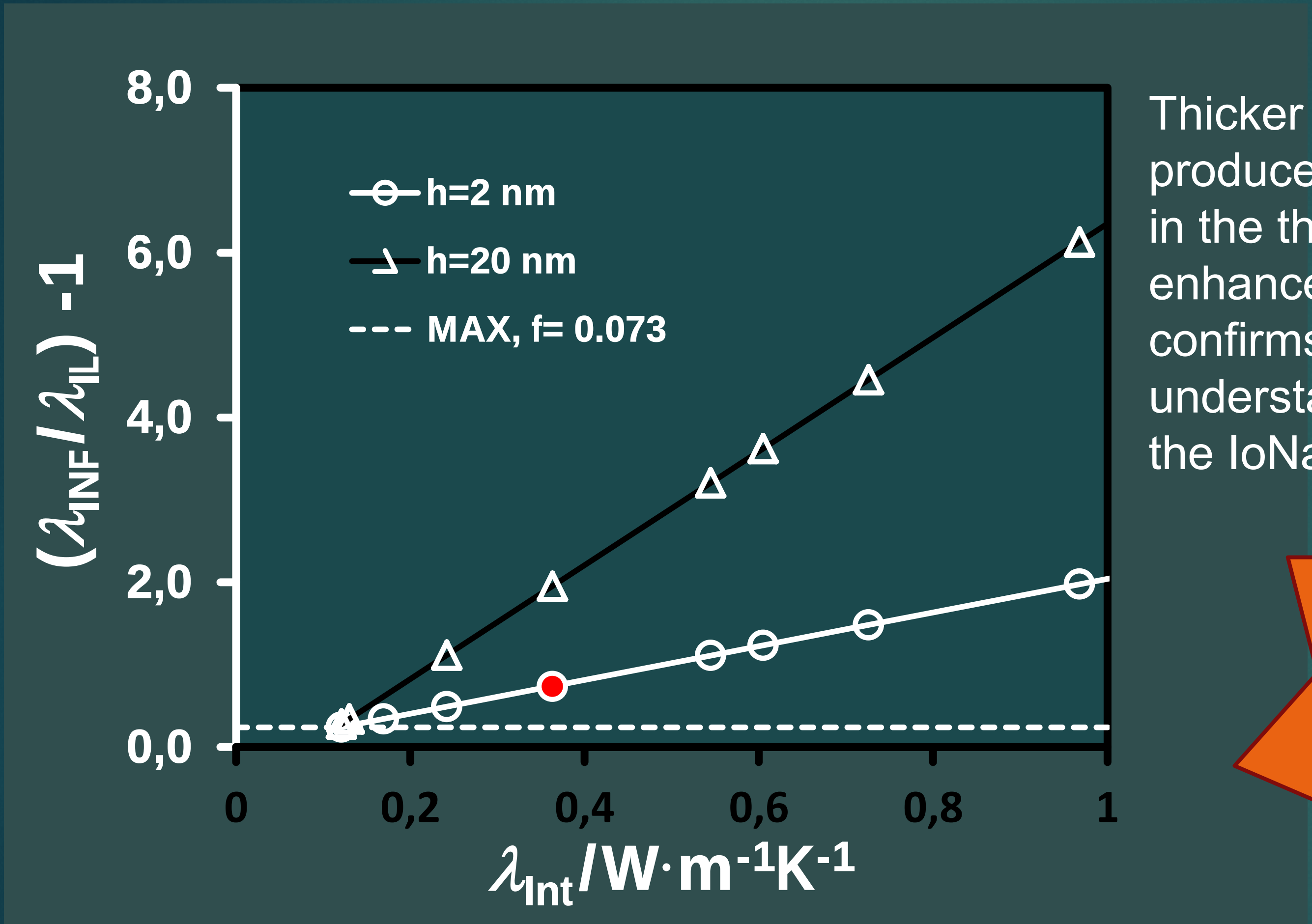


Interface 50-70 nm thick, with long range attraction by the nanotubes. Consistent with theories?

CNT random coil

A P C Ribeiro**, S I C Vieira**, P Goodrich, C Hardacre, M J V Lourenço, C A Nieto de Castro, "Thermal conductivity of $[C_nmim][(CF_3SO_2)_2N]$ and $[C_4mim][BF_4]$ IoNanofluids with carbon nanotubes – Measurement, theory and structural characterization" **J. Nanofluids 2, 55–62, 2013**

Can theories adjust this effect?



Thicker interfacial layer produces a tremendous increase in the thermal conductivity enhancement, a result that confirms the need for a better understanding of the structure of the IoNanofluids

Yes, but generalization is not yet possible

Thermal conductivity enhancement predicted by Leong et al. model, for different values of the thermal conductivity of the interfacial layer. Values for different values of interfacial layer thickness *h* = 2 and h = 20 nm are shown. The **red dot** represents the application to [C_4mim][NTf_2]

J M P França, S I C Vieira, M J V Lourenço, S M S Murshed, C A Nieto de Castro, "Thermal Conductivity of [C_4mim][$(CF_3SO_2)_2N$] and [C_2mim][$EtSO_4$] and their IoNanofluids with Carbon Nanotubes: Experiment and Theory", **J. Chem Eng. Data, 58, 467−476, 2013**

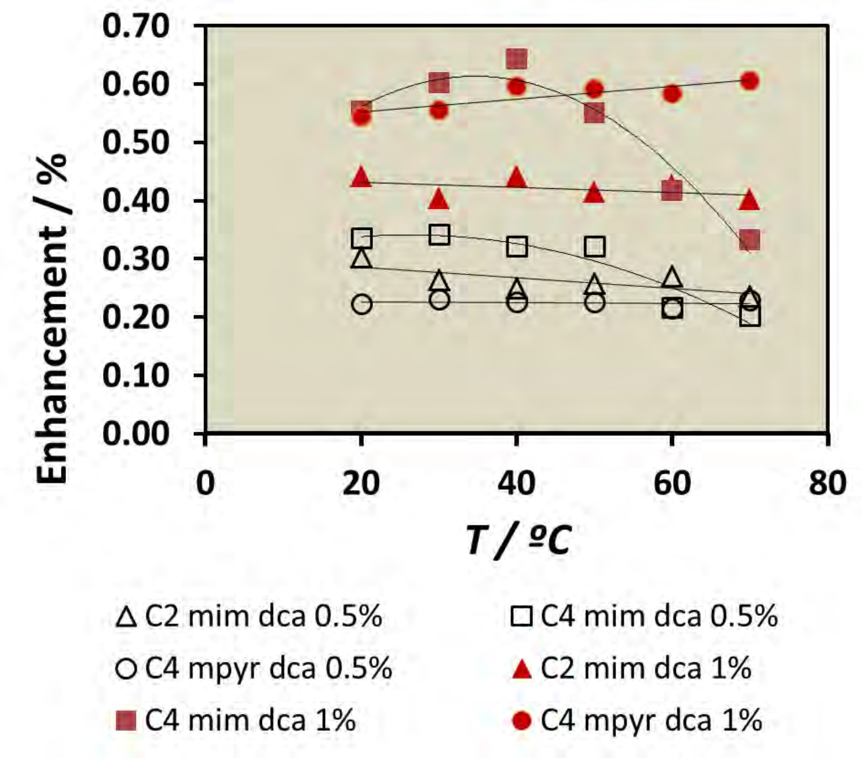
… More Results

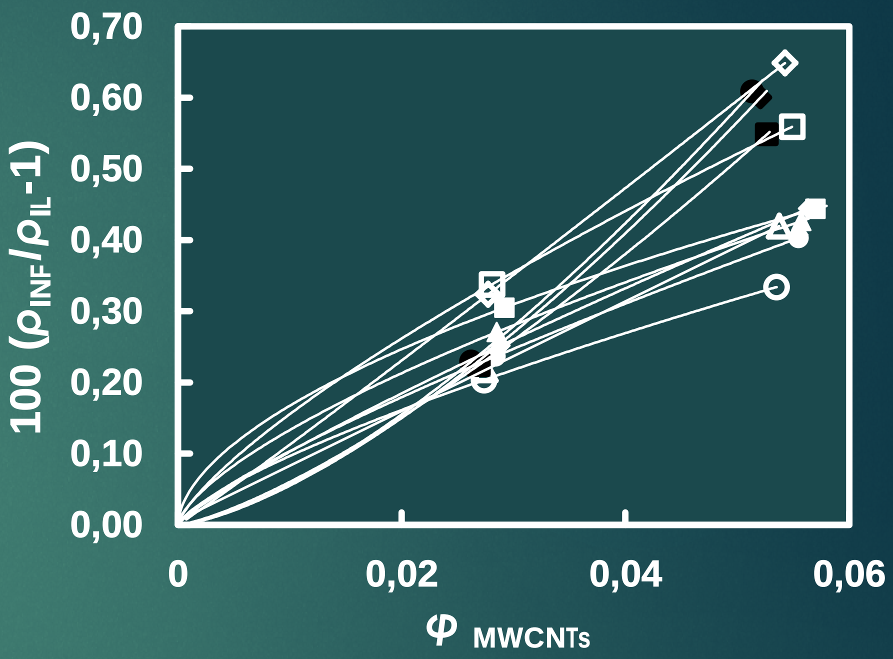
DENSITY, VISCOSITY, HEAT CAPACITY

ENHANCEMENTS?

Density enhancement

Ionanofluids based on $[C_4mim][dca]$, $[C_2mim][dca]$, and $[C_4mpyr][dca]$ as a function of temperature and volume fraction





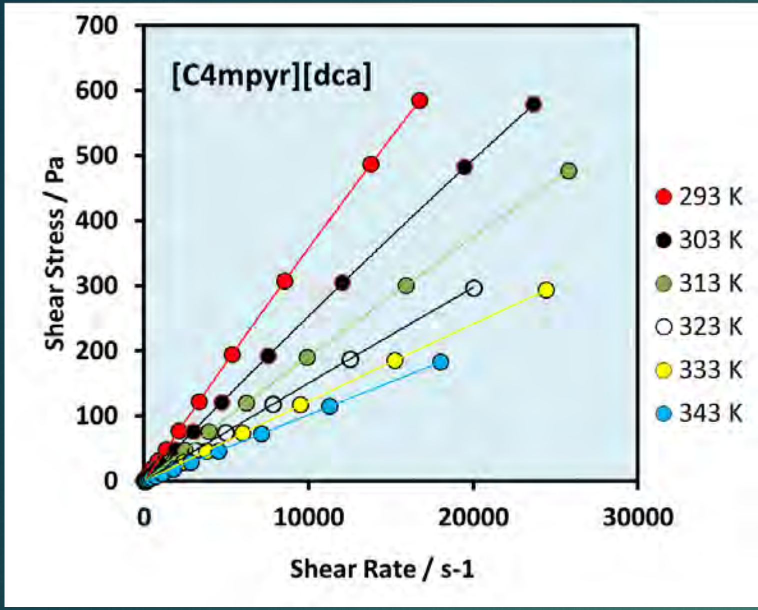
■, □, ■ - T = 293 K; ◆, ◇, ◆ - T = 313 K; ▲, △, ▲ - T = 333 K; ●, O, ● - T = 343 K; Full symbols: - INF based on $[C_2mim][dca]$; Empty symbols: - INF based on $[C_4mim][dca]$; Black symbols: - INF based on $[C_4mpyr][dca]$.

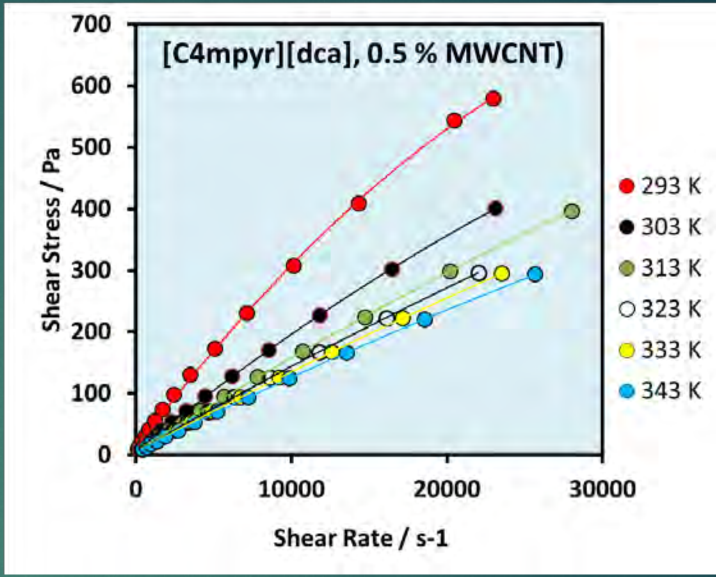
J M P França, F Reis, S I C Vieira, M J V.Lourenço, F J V Santos, C A Nieto de Castro, "Thermophysical Properties of Ionic Liquid Dicyanamide (DCA) Nanosystems", **J. Chem. Thermodynamics, 79 (2014) 248–257**

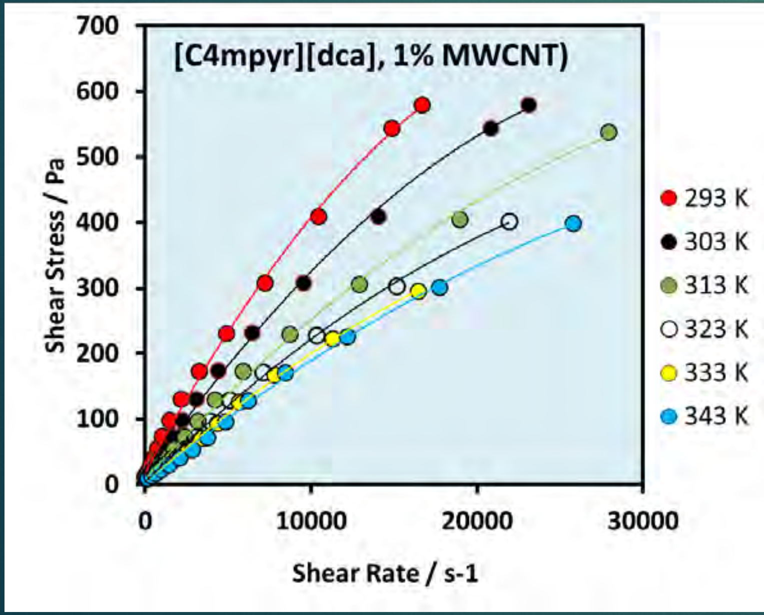
Viscosity

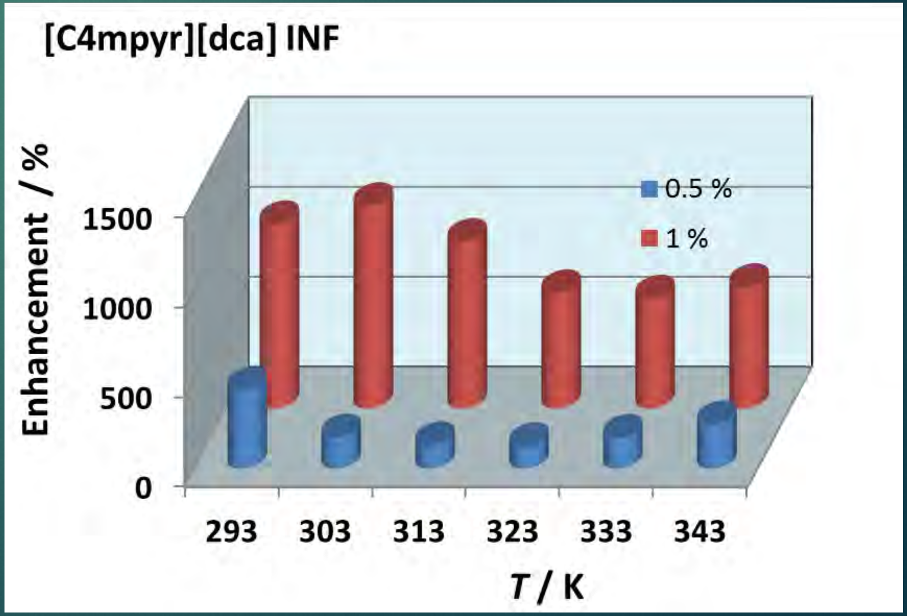
- Ionic liquids are known to be Newtonian liquids – proportionality, in wide ranges of shear stress, between shear rate and shear stress
- **However all the IoNanofluids studied are non-Newtonian**
  - Bingham plastic in behavior - Viscosity appears to be infinite until a certain shear stress is achieved (until a yield stress is overcome)
  - Shear thinning: Viscosity decreases as shear rate/stress is increased (pseudo plastic)

Viscosity

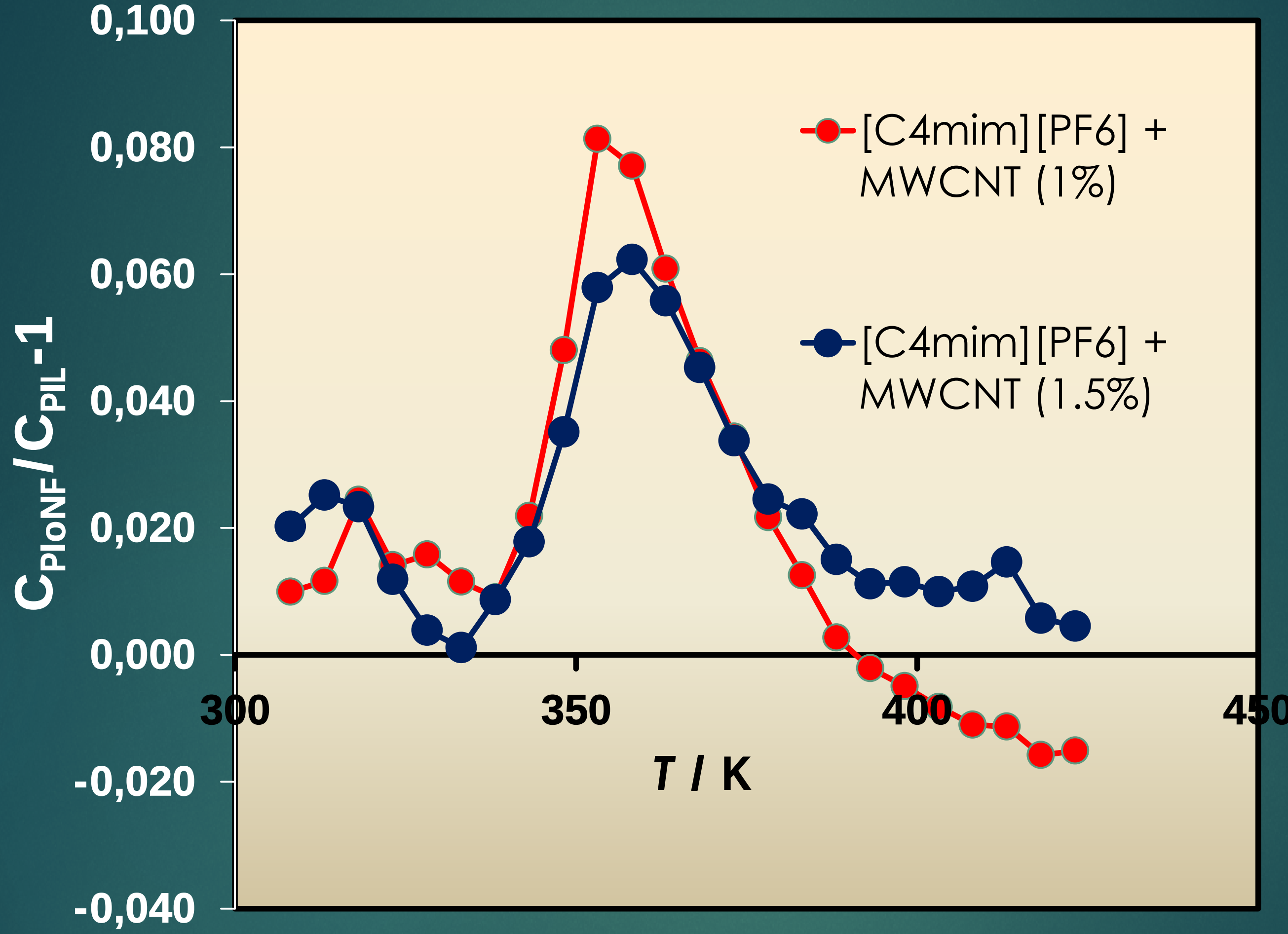

[C4mpyr][dca]
Shear Stress / Pa
Shear Rate / s-1
293 K
303 K
313 K
323 K
333 K
343 K


[C4mpyr][dca], 0.5 % MWCNT)
Shear Stress / Pa
Shear Rate / s-1
293 K
303 K
313 K
323 K
333 K
343 K


[C4mpyr][dca], 1% MWCNT)
Shear Stress / Pa
Shear Rate / s-1
293 K
303 K
313 K
323 K
333 K
343 K


[C4mpyr][dca] INF
Enhancement / %
0.5 %
1 %
T / K

Heat Capacity



Non-analytic behavior? New criticality? Typical in order-disorder phenomena. Existing in liquid-liquid systems! Existing in solid systems!

Challenges

SCIENTIFIC

TECHNOLOGICAL

Challenges - Scientific

- **To measure extensively the properties of IoNanofluids**
- To understand the mechanism of heat transport in complex fluid systems
- **To understand in a deeper way the intermolecular forces and the internal charge distribution in ionic liquids (polar and non-polar domains)**
- To make computer simulations to study structure and dynamics of ionic liquids in contact with carbon nanomaterials (interface), such as graphene sheets and nanotubes
- **To study the stability of micro/nano-emulsions, microphases, clustering, etc.**

Challenges - Technological

- To develop stable emulsions in a long term
- **To design more efficient heat transfer devices**
- To discover the **"best" ionic liquids**, cost/benefit (the price of their industrial production is decreasing to levels that will make them competitive with current fluids used in industry (less than 20 €/kg)
- To discover the **most efficient** nanomaterials
- To analyse the **environmental/regulatory impact**
- Consider sealed and open systems (processing)
- Avoid non-Newtonian fluids
- Materials compatibility with processing equipment
- But…The specific interactions of the ionic liquids with the nanomaterials can alter its individual toxicity

Is it the effort worthy?!...

- Multi-billion markets are open
- Many new products for engineering fluids, heat insulators, catalysts, …, can be envisaged
- Replacement of environment aggressive chemicals, foams, solid composites are in daily order, imposed by regulations or social responsibility
- New challenges open new jobs for chemists, material scientists and engineers

Foreseeing Industrial Applications

THERMAL STABILITY

ECOTOXICITY (IL'S + NANOMATERIALS)

COST

Other process requirements

- In order to use IoNanofluids in industry, other factors have to be considered:
  - **IL thermal stability** - confident that it is easy to target an operational value up to 200°C
  - **IoNanofluid thermal stability** - the thermal stability of the dispersion, on a long term – different game as the homogeneous system can be transformed in a heterogeneous phase, with micro phase equilibria, promoting aggregation of the nanomaterials and/or phase separation, at a micro or macroscopic level.
- Toxicity of IL's, NM and INF

Ecotoxicity

- For ionic liquids, our current knowledge is still scarce, and without long term consequences.
- Currently, only the ionic liquids which have already found application on industrial scale are undergoing REACH registration (EU)
- For nanomaterials, although present in very small quantities, the situation is also not comfortable
- Needs for appropriate ecotoxicity parameters

Ecotoxicity Tests

- Tests were tried *in vitro* to determine LC50 – the average lethal concentration (50% of deaths), after 24 h of contact of LI molecules with *Artemia Salina* eggs (brine shrimp larva), one organism of the marine ecosystems (salted water), with a concentration of 1, 50, 100 and 150 µmol/L
- 4 IL's were test, 4 DCA salts [C_2mim][DCA], [C_4mim][DCA], [C_4mpyr][DCA] and [$P_{6\,6\,6\,14}$][DCA]
- Results are referred here for [C_2mim][DCA], [C_4mim][DCA], [C_4mpyr][DCA]
- Wilson Gouveia et al (2014), to be published

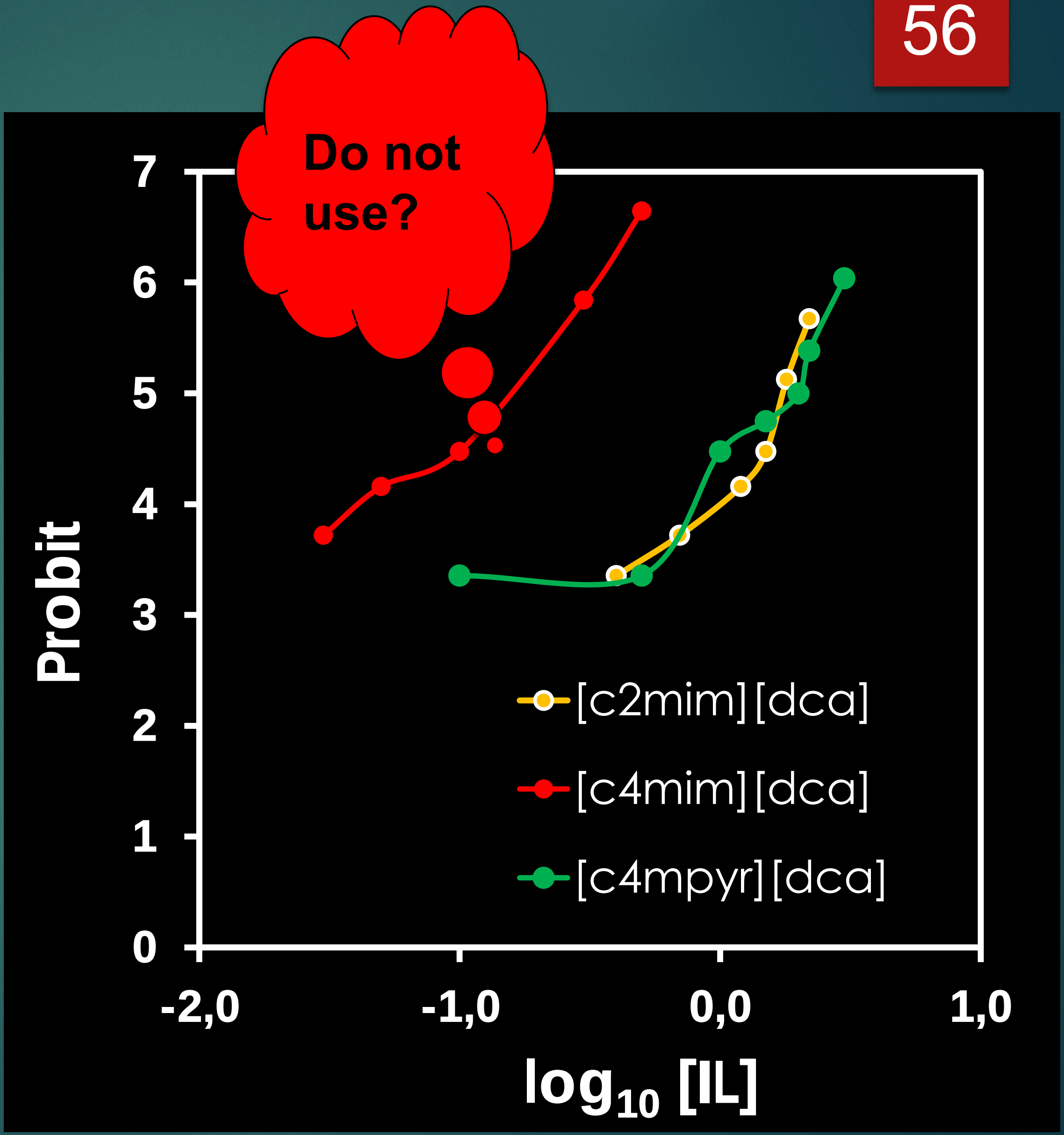
Wilson Gouveia, Filipe Reis, Maria José Lourenço, Eduarda Araújo

(July 2013)

To be published

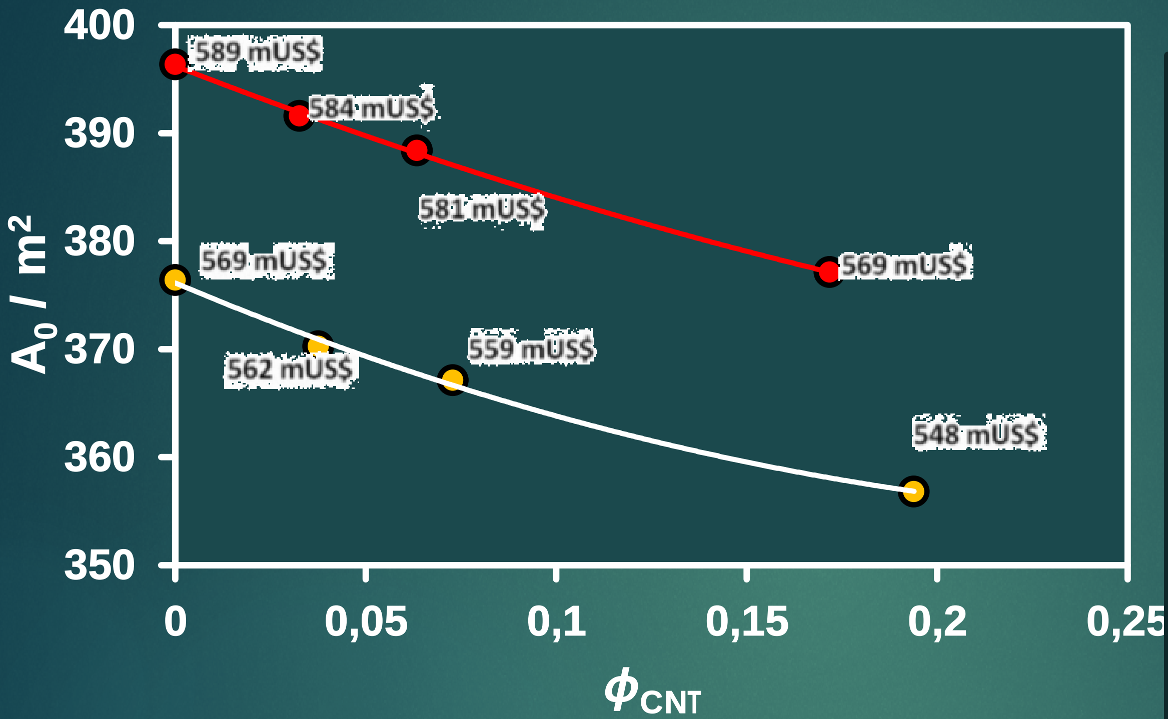
Probit* Analysis

$$\mathrm{probit}(p) = \sqrt{2}\,\mathrm{erf}^{-1}(2p-1)$$



the probit function is the quantile function, i.e., the inverse cumulative distribution function (CDF), associated with the standard normal distribution. Introduced in 1934 by Chester Bliss – the probit model is vey important in toxicology analysis.

And cost?



A_o vs φ_{CNT} for ionic liquids and IoNanofluids. ● - fluids based on $[C_4mim][NTf_2]$; ● - fluids based on $[C_2mim][EtSO_4]$. Close to each data point is the cost of the heat exchanger, in mUS$

The effect, only of the thermal conductivity enhancement **can be as much as 20% decrease in the area of heat transfer**, and therefore in the cost of a shell and tube heat exchanger, saving about US$ 20 m for a 20% volume fraction of MWCNT (3% w/w), **a very significant value**

Carlos Nieto de Castro, Ana P. C. Ribeiro, Salomé I.C. Vieira, João M. P. França, Maria J.V. Lourenço, Fernando V. Santos, S. M. S. Murshed, P. Goodrich and C. Hardacre, *"Synthesis, properties and physical applications of IoNanofluids"*,
Chapter 2 in Ionic Liquids - New Aspects for the Future, Ed. Jun-ichi Kadokawa, INTECH, 2013

Current Applications

- New Engineering Fluids
  - Heat transfer fluids (HTF's) for heat exchangers
  - Heat transfer fluids for boiling and condensation
  - New absorbing refrigeration fluids
- New paints for solar absorbing panels
- Insulation panels
- New nanocatalysts

Pay attention to	
	Nanomaterial: Size, Characterization, Purity, Shape, Composition, Surface chemistry, including the surface coating material, Manufacturing process.
	Their choice can contribute to diverse ecological/toxicological properties, purity, product variability, performance and use.
	Method of dispersion.
	Essential requirements: stability over a long period of time, durability of the suspension, prevention of agglomeration and the constancy of the fluid chemistry.

Pay attention to	When publishing, indicate if surfactants were used, materials with surface coatings, dispersion parameters, contaminants, amount of water in the nanofluid, when properties measurement were made after the dispersion, etc. These parameters influence thermal conductivity, heat capacity, viscosity, etc.
	Toxicological studies.

Challenges to IoNanofluid Research

1. Long-term stability without adding dispersants

2. Proper sample preparation and reliable measurements

3. Thermodynamics formulation (Gibbs) of multiphase heterogeneous systems (dispersions)

4. Understand heat transfer mechanisms

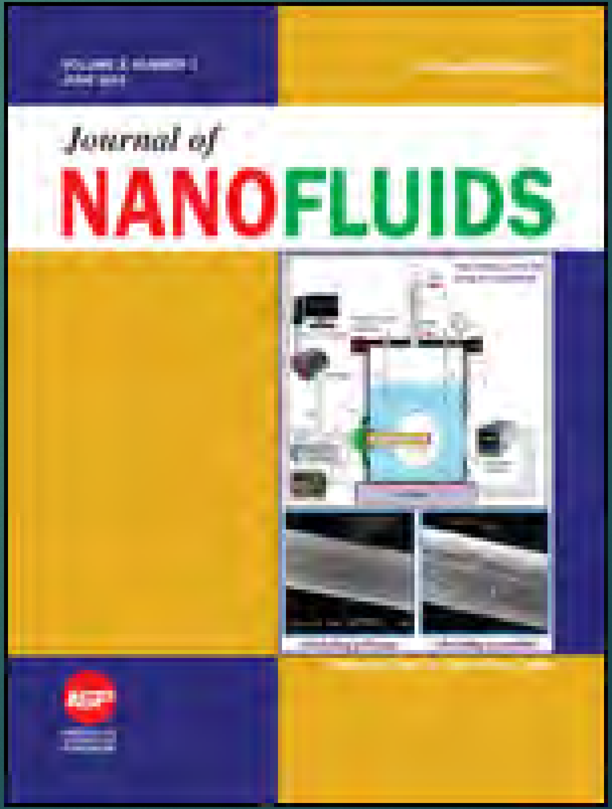
5. Molecular simulations of IL-nanomaterial interface

6. Characterization of the particles/clusters in the nanofluid

Two announcements

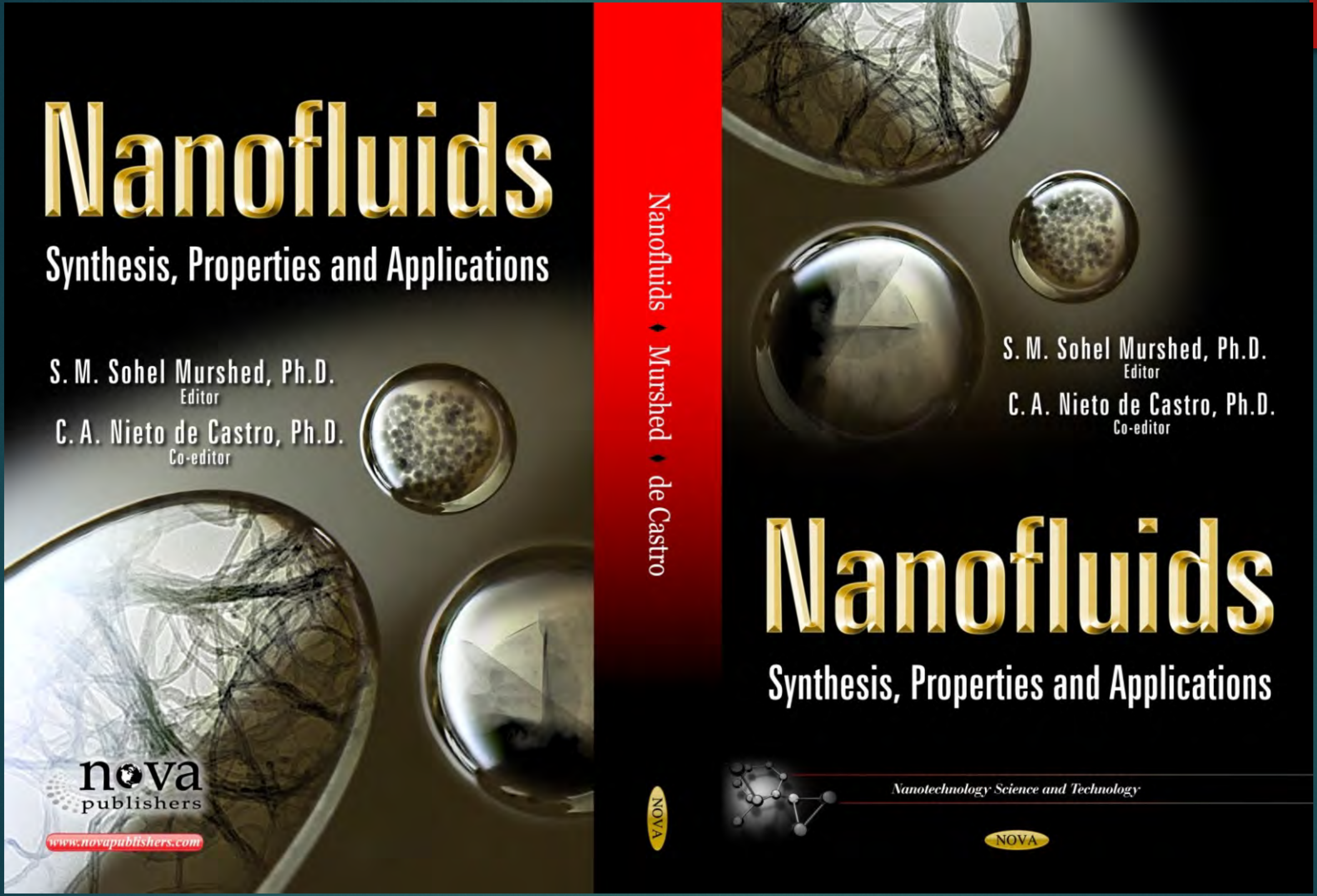
- New Journal in the area – **Journal of Nanofluids** http://www.aspbs.com/jon/
- Launched in 2012

Sohel Murshed – Editor
Carlos Nieto de Castro – Member Editorial Board



AMERICAN SCIENTIFIC PUBLISHERS

New Book



NOVA Science Publishers, Inc., New York, (2014)
ISBN (978-1-63321-677-8); https://www.novapublishers.com/catalog

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- PTDC/QUI/66826/2006
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FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

SEVENTH FRAMEWORK PROGRAMME

NARILAR

MARIE CURIE ACTIONS

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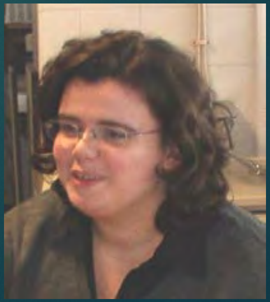
Maria José Lourenço

Sohel Murshed

Salomé Vieira

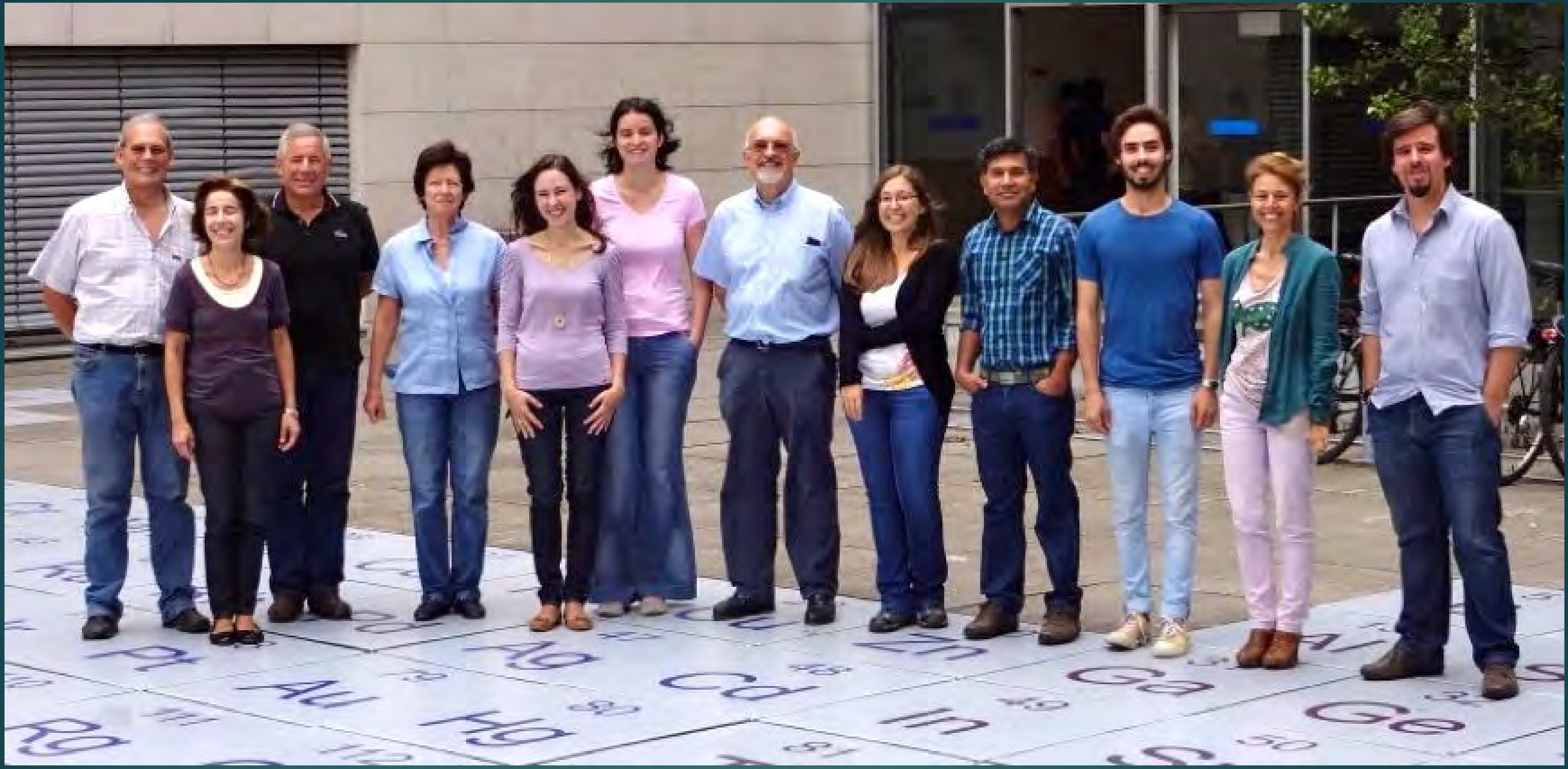
João França

Fernando Santos



Ana Paula Ribeiro

Molecular Thermophysics and Fluid Technology (MTFT)



http://groups.ist.utl.pt/~cqe.daemon/members-contacts/research-groups-2/205-2/

CQE
Química Estrutural

MOLECULAR THERMOPHYSICS AND FLUID TECHNOLOGY

Thematic Area: Thermodynamics of Fluids and Nanosystems

Thematic Line 4 - Thermodynamics of Fluids and Nanosystems

CQE Química Estrutural

MET (IST)
Molecular and Engineering Thermodynamics

MTFT (FCUL)
Molecular Thermophysics and Fluid Technology

ENGINEERING AND SUPERCRITICAL FLUIDS

- Characterization of novel engineering fluids under normal and extreme conditions
- Standard Reference Data and Fluids
- Extraction, reaction and micronization in Super Critical Fluids (SCFs)

SURFACE STUDIES

- Self-organized films
- Controlled drug release
- Bio-implant rheology
- Novel hydraulic binders

IONIC LIQUIDS

- IL modeling and force-field development
- Interactions between ILs and carbon nanomaterials
- IL transport properties
- Molecular dynamics in ionic nanoclusters

NEW SENSORS AND INSTRUMENTS

- Molecular mechanisms of heat transfer in nano and IoNanofluids
- Technological applications and technology transfer

Crossing Themes

Functional Materials	Energy Storage	ILs and APIs
SCFs, ILs and NM in Catalysis	Drug Delivery and Stability	IL Synthesis

Students (MSc, PhD), Post-Docs

- Many projects are undergoing
  - Heat transfer fluids
  - Solar energy efficiency
  - Absorption refrigeration
  - Nanocatalysis
  - …

- WELCOME!

- Contact cacastro@ciencias.ulisboa.pt

- Condition: To love Ionic Liquids, Nanomaterials or Engineering Fluids!

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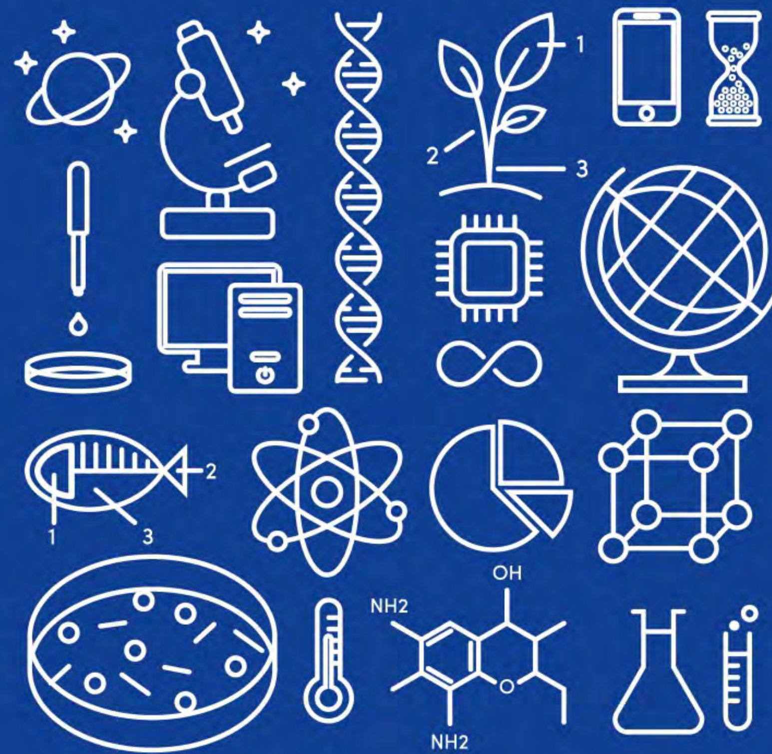

www.ciencias.ulisboa.pt

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"O que hoje não sabemos, amanhã saberemos" Garcia de Orta, 1563

Market of nanomaterials

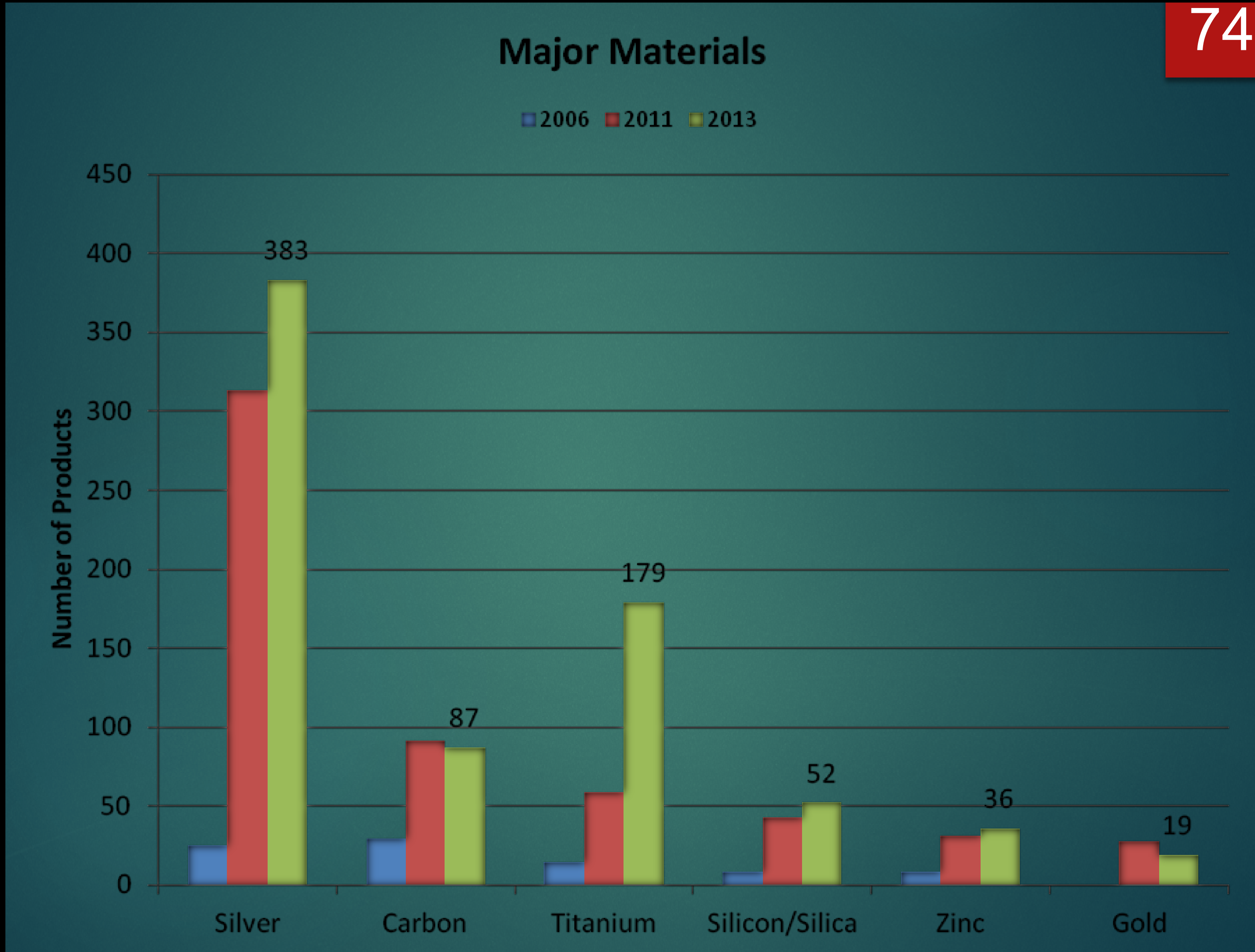
Global market: 11 million tonnes **Market value: €20 billion**
Direct employment: 300 000 to 400 000 in Europe

Strengths of universities spin-out companies	R&D made in universities
	Cutting edge work
	Large companies delegate/invest in smaller companies the commercialization of radical innovative products
Barriers	High level market and technological uncertainty
	Large scale
	Long term investment
Fails of universities spin-out companies	Accessing the right strategy
	Identifying the rapidly emerging trends in the market
	Nanomaterials' properties/applications open promising areas, which difficult the prioritization of objectives

Nanomaterials characterization

Nanomaterials in REACH registrations

	2010	2013	Non phase-in
Substance name	1. Carbon black 2. CeO_2 3. $CaCO_3$ 4. ZnO 5. Ag	1. MWNT 2. Graphite 3. TiO_2 4. F_6-Si.2Na reaction products with $LiMg_4Na_3(Si_{12}O_{30})$	1-4 Names claimed confidential under NONS


Major Materials
2006
2011
2013
Number of Products
450
400
350
300
250
200
150
100
50
0
383
87
179
52
36
19
Silver
Carbon
Titanium
Silicon/Silica
Zinc
Gold

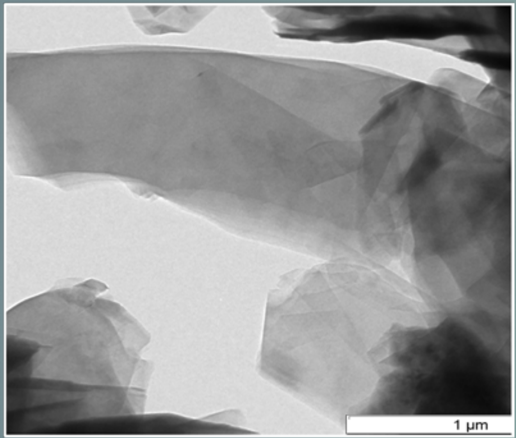
Suppliers

Powder, grain size≤100nm, purity≥99%, most sold/studied by our research group (**Ag**, Ti, TiO_2, CNT, fullerene, graphene, Si, SiO_2, Zn, ZnO_2 and Au).

Supplier	Country	Supplier	Country
Advanced Nanopower	China	Nano Pars Spadana	Iran
American Dye Source	Canada	Nano Powder R&D Center	China
Anderlab	India	Nano-C	USA
Applied Nanotech Holdings	USA	NanoAmor	USA
Catalytic Materials LLC	USA	Nanophase	USA
EMFUTUR Technologies	Spain	NanoIntegris	Canada
EPRUI	China	NeoTechProduct Research	Russia
Goodfellow	England	NTbase	South Korea
Grafen Chemical Industries	Turkey	PlasmaChem	Germany
Graphene Supermarket	USA	PNF	Iran
HeJi	China	SES Research	USA
HZ NANO	China	Sisco Research Laboratories	India
Inframat Advanced Materials	USA	SkySpring Nanomaterials	USA
Intelligent Materials Pvt.	India	Stanford Advanced Materials	USA
IoLiTec	Germany	Sukgyung AT	South Korea
Kemix	Australia	Sun Innovations	USA
Meliorum Technologies	USA	TCI Chemicals	Japan
MER Corporation	USA	Term USA	USA/Russia
MKnano	Canada	Timesnano	China
MTR	USA	XG Sciences	USA
NaBond	China		

Large databases about nanomaterials: Project on Emerging Nanotechnologies CPI and Nanowerk.

Nanomaterials used by our group



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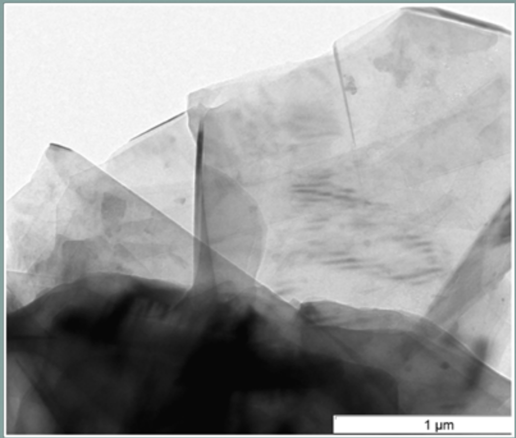
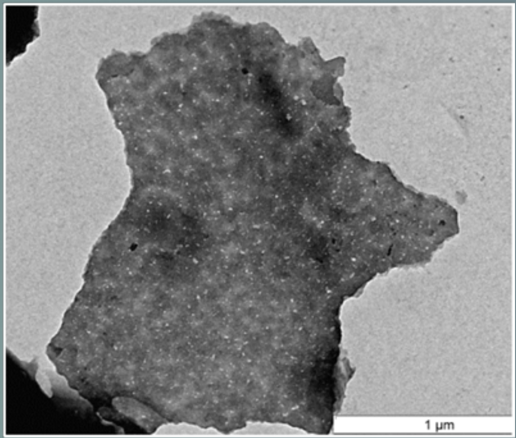
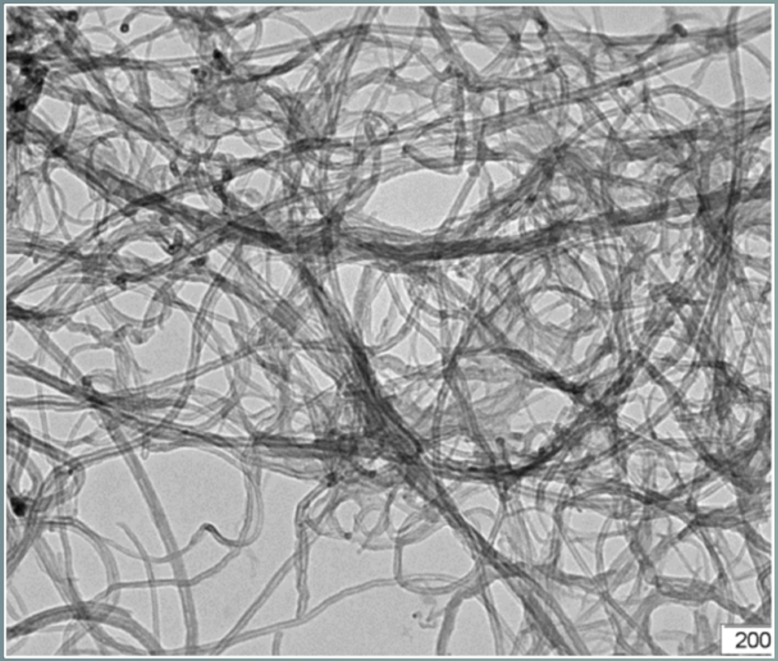


Graphene: image not provided by supplier

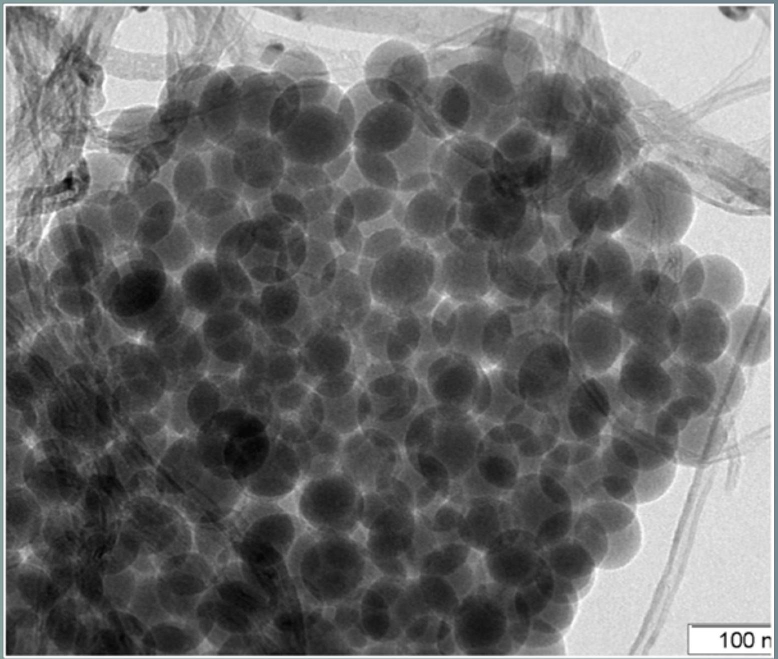


Graphene after ultrasonic probe

Nanomaterials used by our group



CNT 95%



CNT 95% impurities (nanosize)