Microwave assisted synthesis of nanoparticles: from magnetic to fluorescent materials

UNIVERSITÀ DI PISA

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Consiglio Nazionale delle Ricerche
Area della Ricerca di Pisa

Outline

- **Introduction**
  - **The coaxial microwave technology to assist chemical processes**

- **Materials synthesis and characterization**
  - **Metal Nanoparticles (Ag,**
  - **Magnetic nanoparticles (IONs, IONs-HNTs)**
  - **Silicon based quantum dots**

Introduction

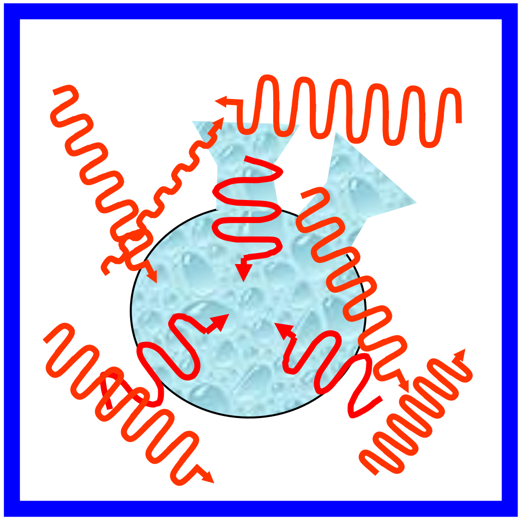
Microwave Assisted Processes

MW assisted chemistry significantly reduces the processing time, energy costs and equipment size compared to the conventional methods

a) Oven type approach

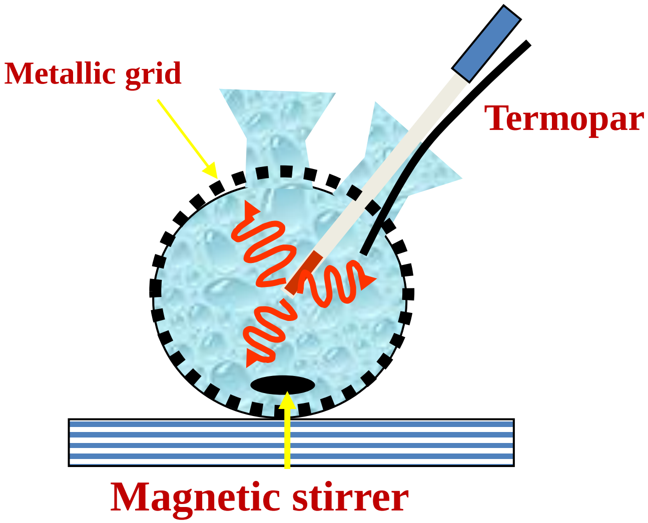
The MW oven-type reactors have two main drawbacks:

- **High equipment cost**
- **Difficult process scale-up**



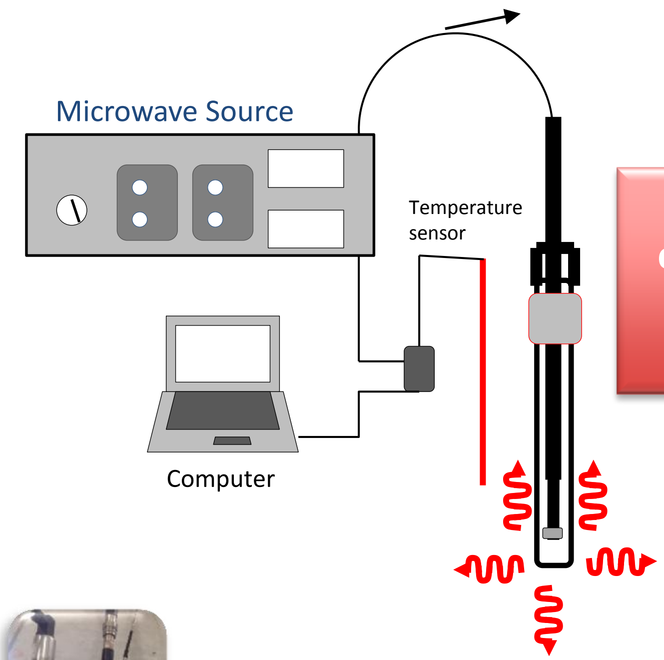
b) Coaxial anntena to apply MW in situ

- **direct manual/visual/instrumental control of the reaction**
- **use ordinary glassware, metal vessels/ no vessel**
- **Easy scale up and safe operation**
- **Simultaneous use of MW, US and UV irradiation**

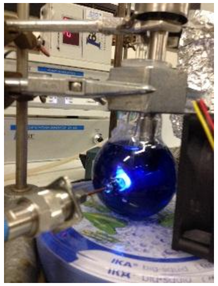


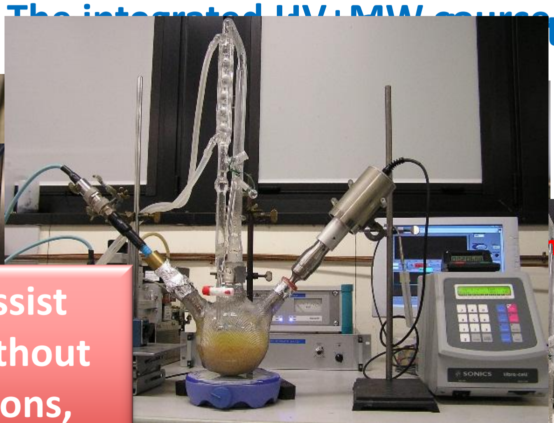
Introduction

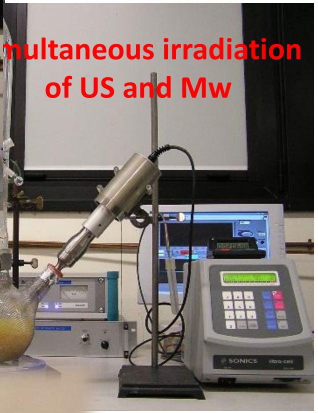
Coaxial Microwave Assisted Processes developments

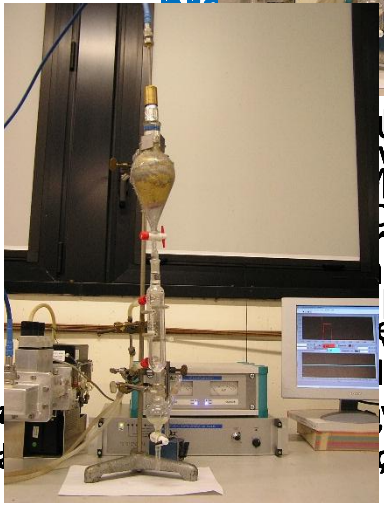


The versatility to assist chemical process without limits in configurations, materials, sensors, etc

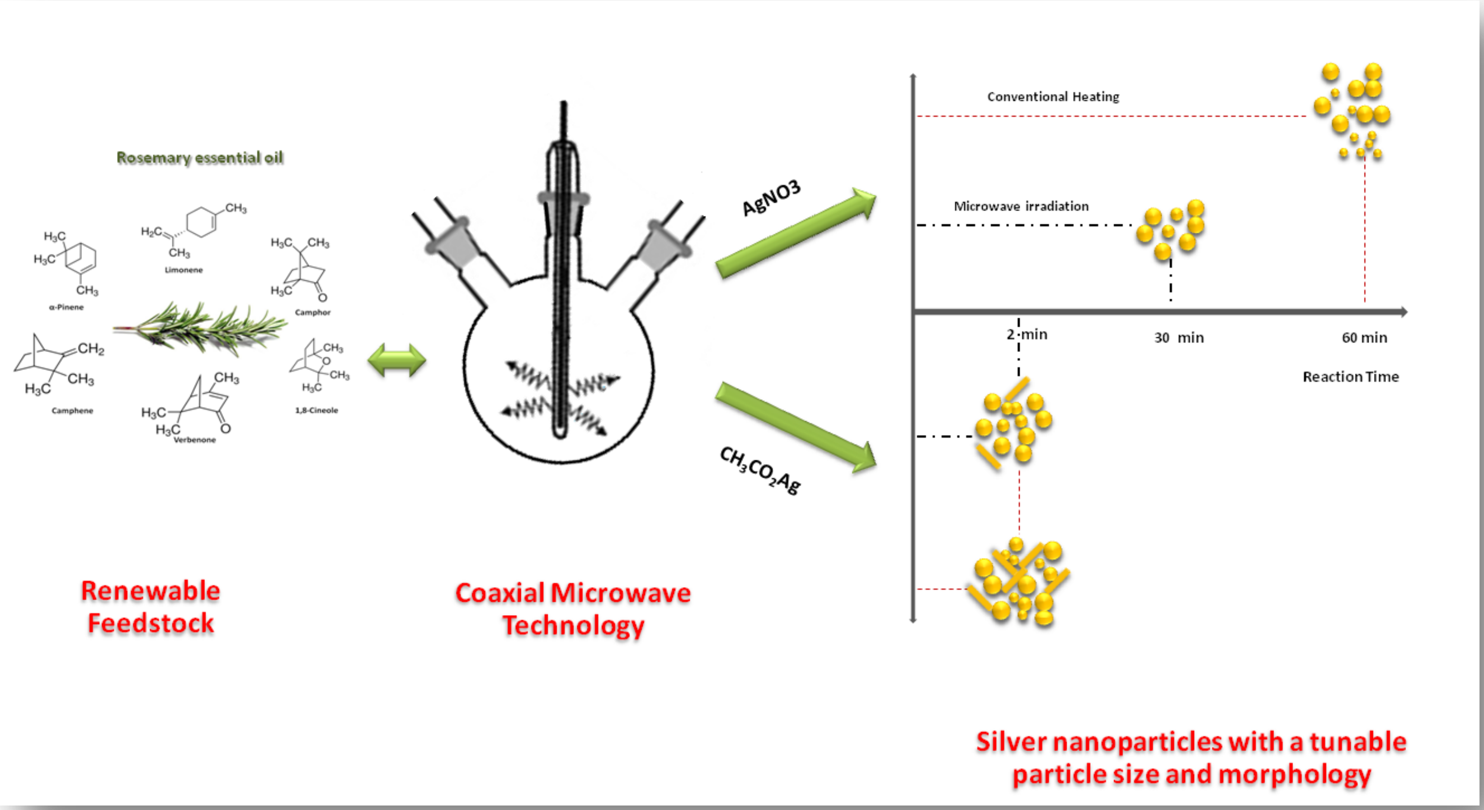








Synthesis of Ag-NPs



Synthesis of Ag-NPs

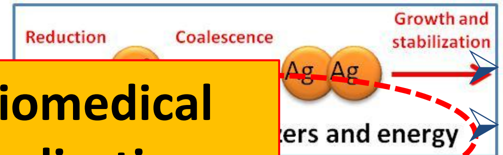
Synthesis of Ag-NPs

Silver

Nanoparticles

Green synthesis → Three key factors

1. Water as solv
2. Bioresources (medicinal plants)
3. Energy?



Biomedical applications

- Antibacterial
- Antifungal
- Antiviral

Bottom-up Approaches

Build up

Top-down Approaches

Enviromental applications

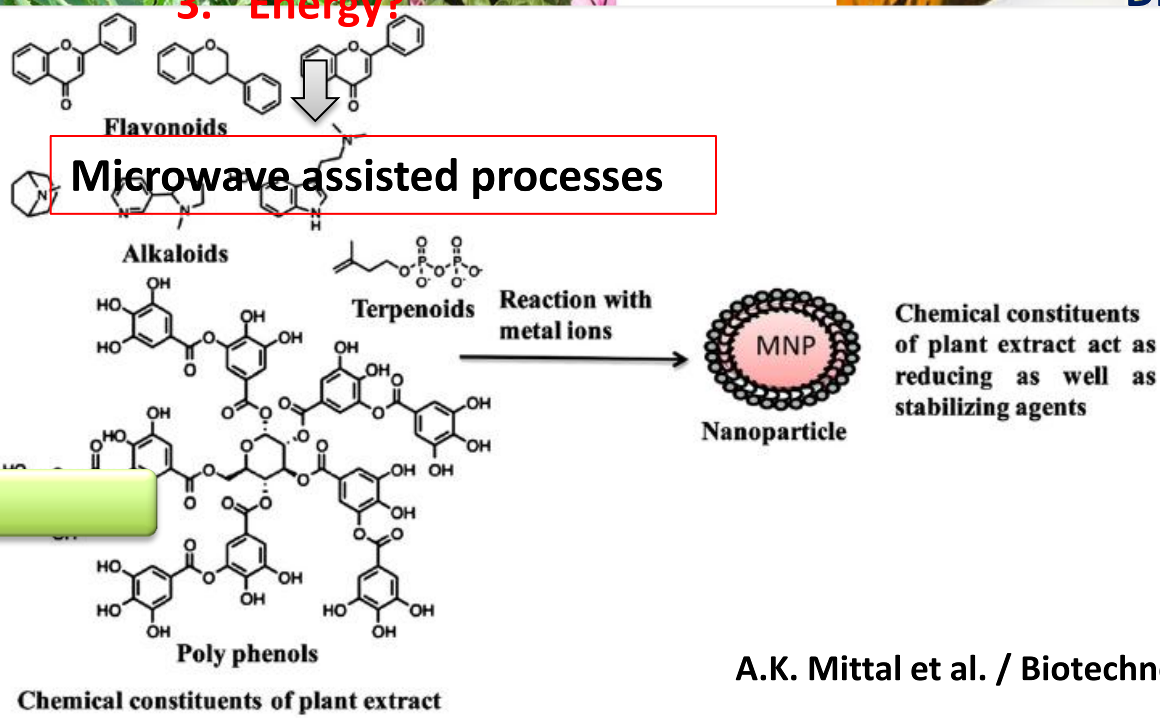
- Catalysts for water and air Disinfection

Aqueous extracts

Algae

Plants

Microwave assisted processes



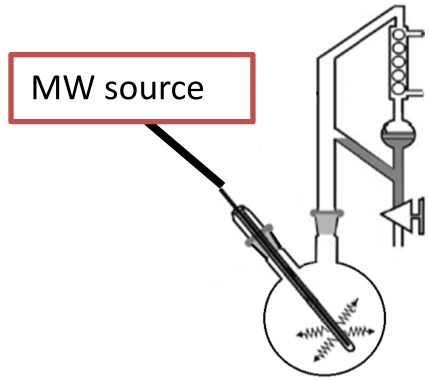
A.K. Mittal et al. / Biotechnology Advances, 2013

m, Green Chem., 2011

Synthesis of Ag-NPs

Rosemary
- native Mediterranean herb
- antibacterial, antioxidant properties and antifungal activities

1)



MW assisted Hydrodistillation

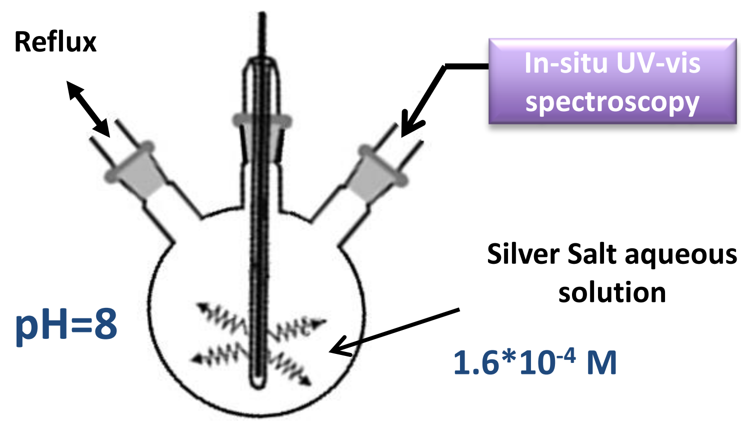
Rosemary essential oil

renewable reducing agent

Chemical composition by GC, GC-MS analysis

6 uL/mL of EO

2)



MW assisted silver nanoparticles synthesis

Ag NPs

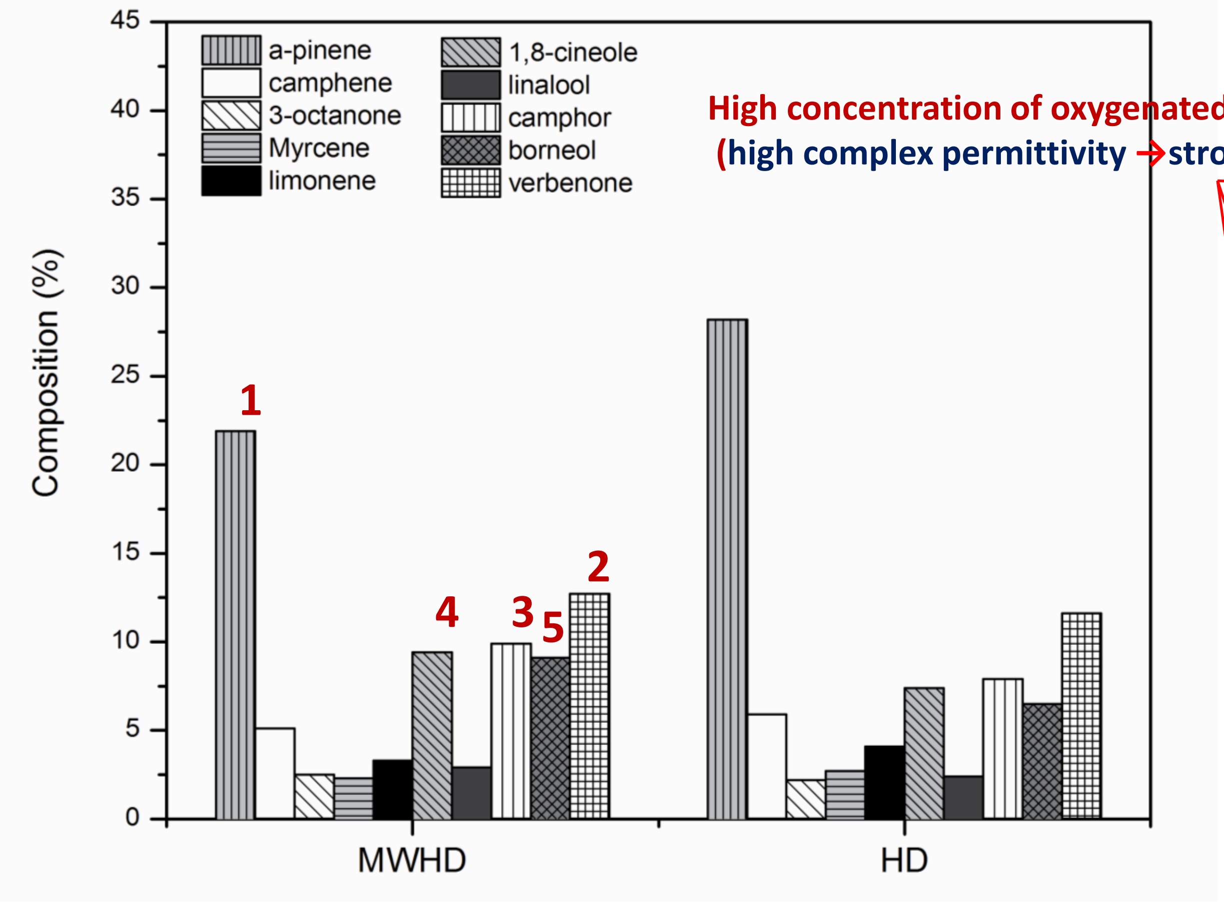
Particle size by SEM image

Synthesis of Ag-NPs

New reducing agent

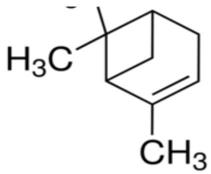
Rosemary Essential Oil Extraction

➡ 29 identified volatile compounds which represent 98.0%,



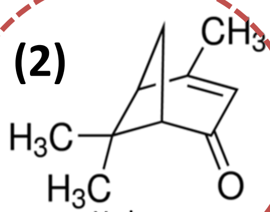
High concentration of oxygenated monoterpenes (high complex permittivity → strong MW interaction)

(1)



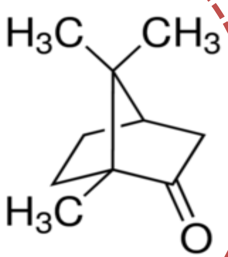
α-Pinene

(2)



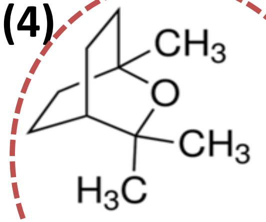
Verbenone

(3)



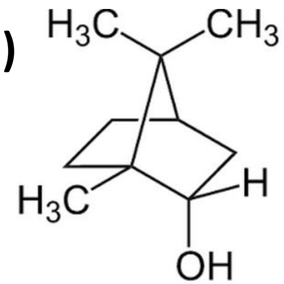
Camphor

(4)



1,8-Cineole

(5)

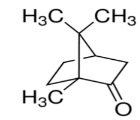


Borneol

*González-Rivera, et al. / Innovative Food Science and Emerging Technologies (2016)

Synthesis of Ag-NPs

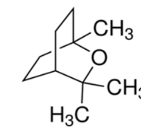
Silver Nanoparticles Synthesis



Camphor

Rosemary ESSENTIAL OIL bio-compounds are ketones, ethers and alcohols

…n time	Particle size	morphology
…n	12 ± 2 nm	spherical
…n	21 ± 7 nm	spherical,

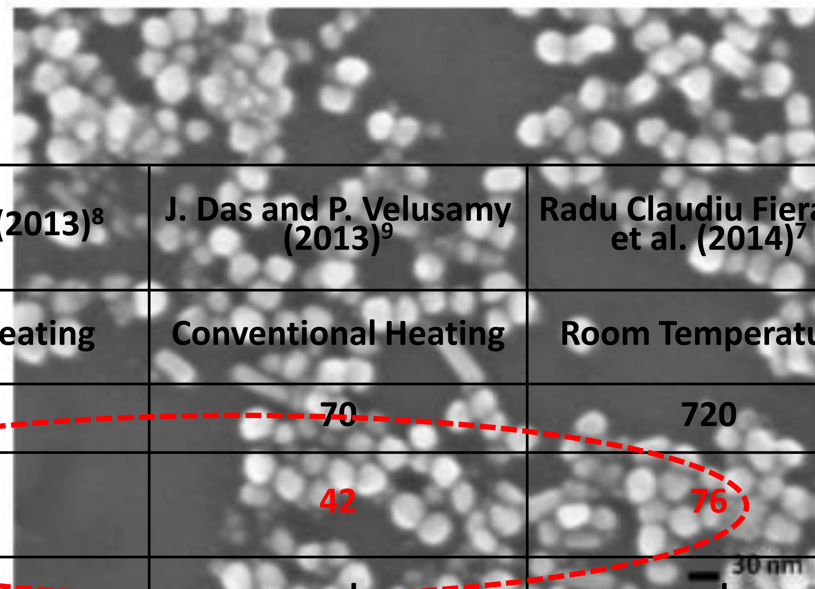


1,8-Cineole

*González-Rivera, et al. /JCTB (2016) submitted

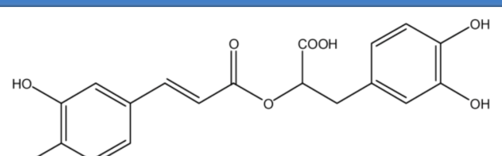
VS

…xtracts

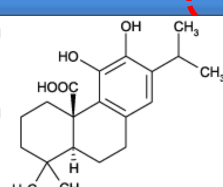


…iman, et al (2013)[8]	J. Das and P. Velusamy (2013)[9]	Radu Claudiu Fierascu et al. (2014)[7]
…ventional heating	Conventional Heating	Room Temperature
30	70	720
60	42	76
n.d	n.d.	n.d.

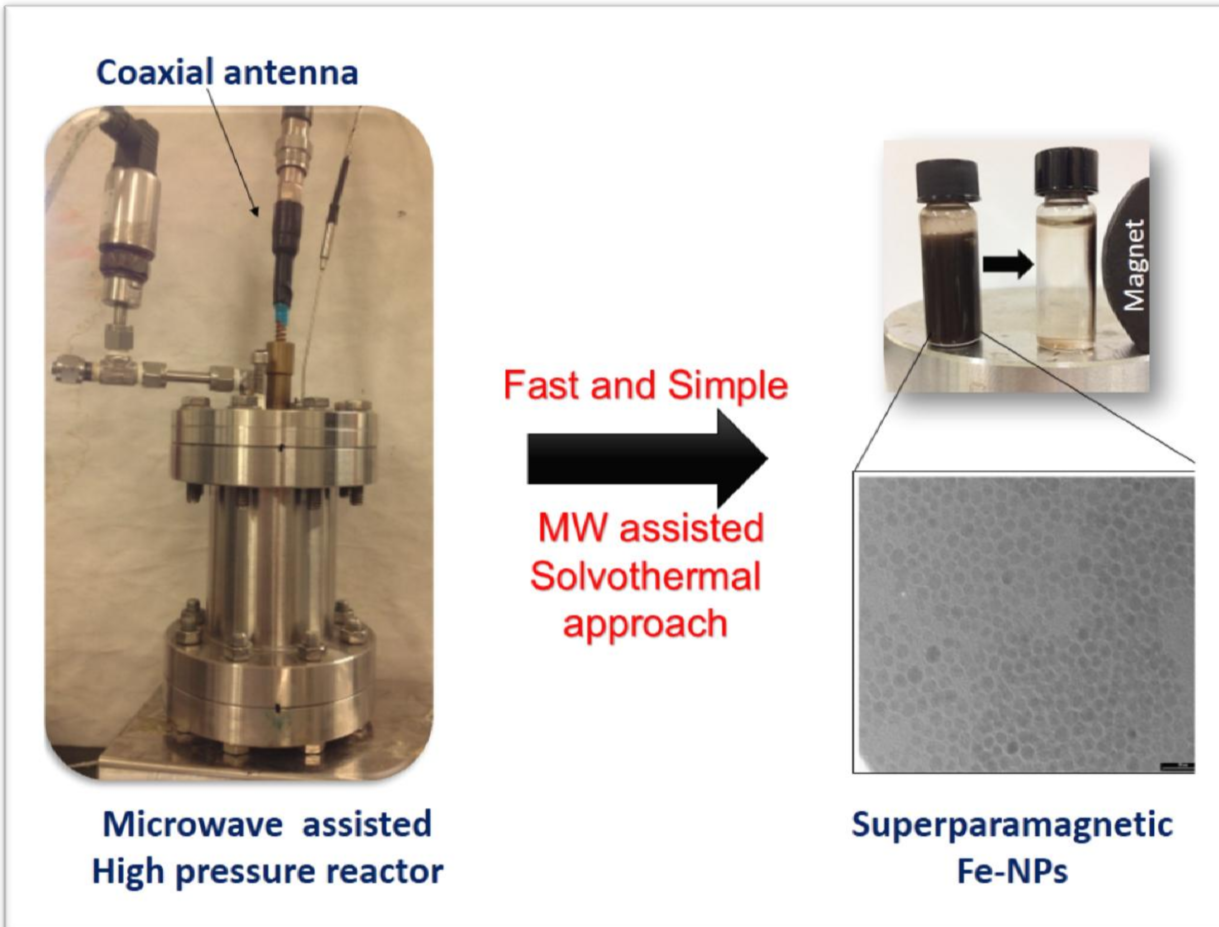
Rosemary AQUEOUS EXTRACTS bio-compounds are proteins/enzymes, aminoacids, polysaccharides, alkaloids, alcoholic compounds, and vitamins could be involved in bioreduction



Rosmarinic acid

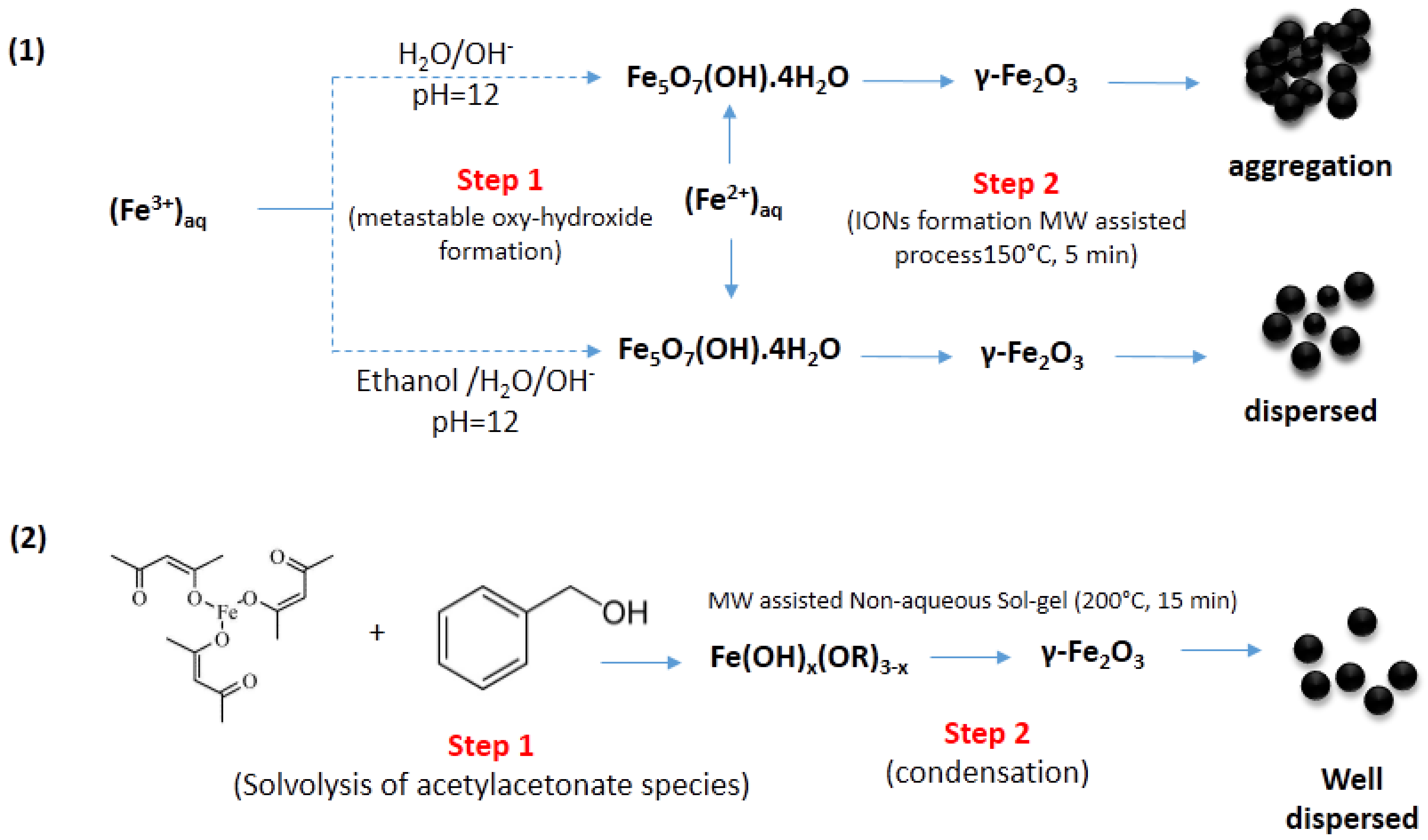


Synthesis of IONs

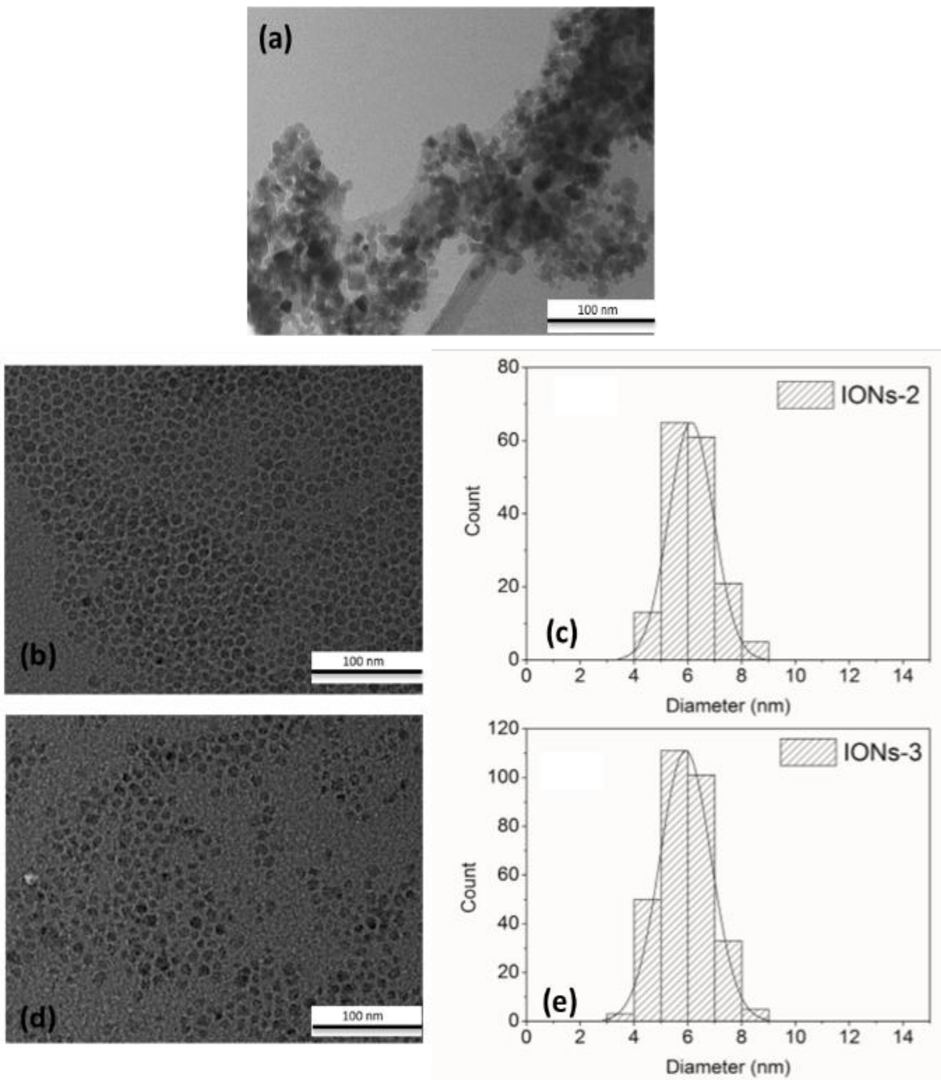


Superparamagnetic IONs

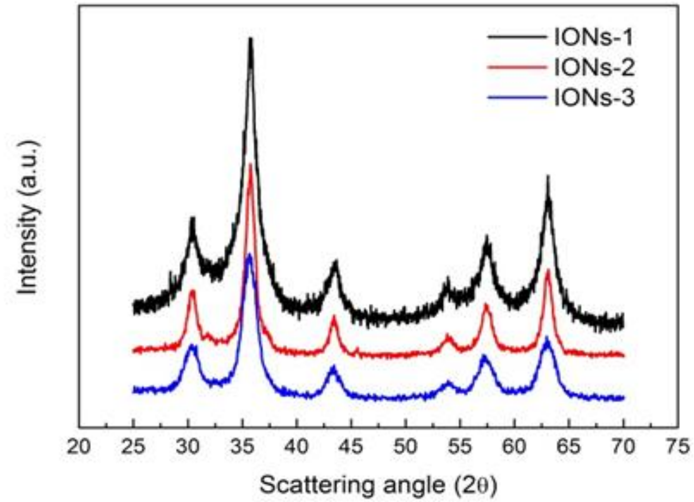
Two different syntheses approaches:



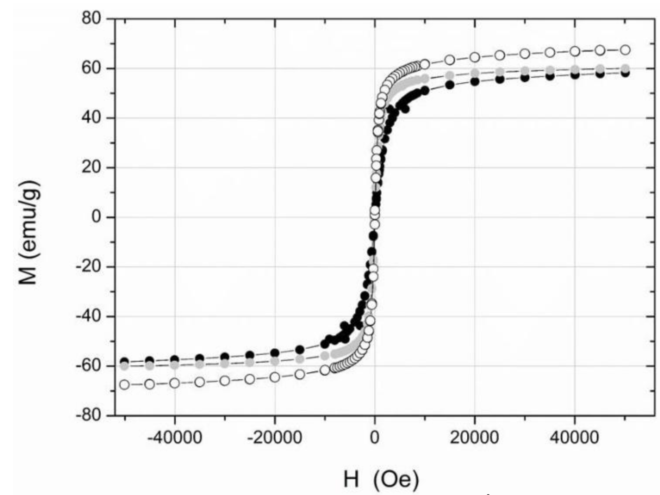
Superparamagnetic IONs



TEM images of magnetic nanoparticles IONs-1 (a), IONs-2 (b) and IONs-3 (d) and histograms of the particle size distribution of IONs-2 (c) and IONs-3 (e).



X-ray powder diffraction patterns for IONs samples.



Trend of the magnetization M (emu/g Fe_2O_3) measured at T=300 K as a function of the external magnetic field H (kOe). Symbols -○-, -●- and -●- refer to IONs-1, IONs-2 and IONs-3, respectively.

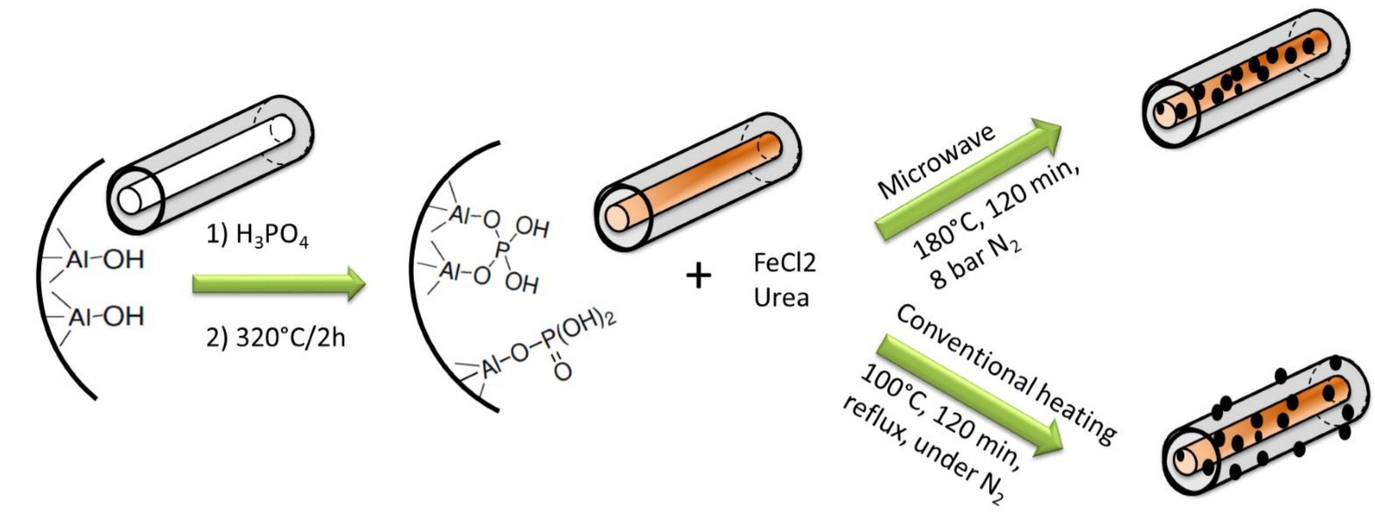
Superparamagnetic IONs

Table 1 Reaction p...
surface coating of

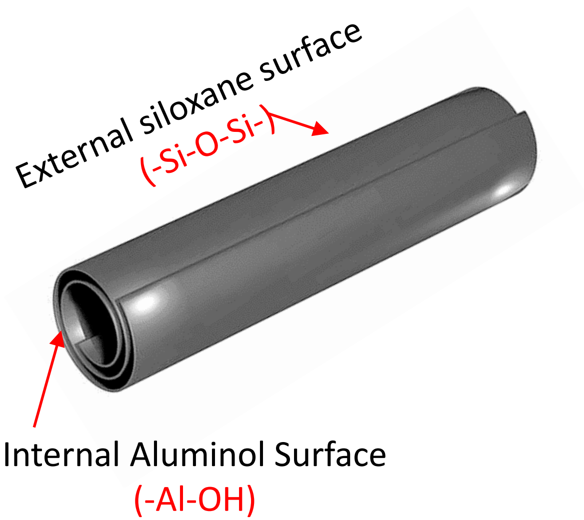
The proposed methodologies produced IONs with physicochemical characteristics that are in line with the best literature results.

MW synthesis	Iron Salt precursor	Temp. (°C)	Time (min)	Solvent	Iron oxide Crystal Phase	Particle Size (nm)	Ms (emu/g) T=300K	Surface coating	Ref.
Hydrothermal	$FeCl_2$	200	6	Ethanol/water (1:2)	Fe_3O_4	22	*N.R.	bare	20
	$FeCl_3$				α-Fe_2O_3	49-91		bare	
	$FeCl_2/FeCl_3$				Fe_3O_4/γ-Fe_2O_3	17		bare	
	$FeCl_2/FeCl_3$ (IONs-2)	150	5	Ethanol/water (1:2)	γ-Fe_2O_3	6.1±0.8[1] 6.9[2] 7.2[3]	60	bare	this work
	$FeCl_2/FeCl_3$	60	120	Water	Fe_3O_4/γ-Fe_2O_3	13.5	72.9	Citric acid	15
	$FeSO_4$	85	30	Water	Fe_3O_4/γ-Fe_2O_3	13.8	72	bare	50
	$FeCl_3$	220	25	Water	α-Fe_2O_3	100	*N.R.	Phosphate[b]	33
	$FeSO_4/FeCl_3$	150	25	Water	γ-Fe_2O_3	10	40	bare	34
	$FeCl_3$	100	10	Water	Fe_3O_4/γ-Fe_2O_3	30-50	60	Dextran	9
	$FeCl_2/FeCl_3$ (IONs-1)	150	5	Water	γ-Fe_2O_3	----[a] 6.9[2] 7.3[3]	68	bare	this work
Non-aqueous Sol-gel	$Fe(acac)_3$	180	10	Benzyl alcohol	γ-Fe_2O_3	7.2	60	Citrated	35
	$Fe(acac)_3$	160	5	Benzyl alcohol	Fe_3O_4/γ-Fe_2O_3	5.4	60	Oleic acid	36
	$Fe(acac)_3$	200	240	Benzyl alcohol	Fe_3O_4/γ-Fe_2O_3	7.4	*N.R.	N.R.	38
	$Fe(acac)_3$	200	15	Benzyl alcohol	Fe_3O_4	5.4	42.5	Benzoate[b]	48
	$Fe(acac)_3$	200	15	Benzyl alcohol	γ-Fe_2O_3	5.5±0.9[1] 4.7[2] 5.4[3]	63	Benzaldehyde[b]	this work
Others solvothermal	$FeSO_4$	80	240	Cyclohexane/1-pentanol/water	α-$Fe2O_3$	270-310	0.104	bare	42
	$FeCl_3$	160			α-Fe_2O_3	120	0.011	bare	
	$FeCl_3$	200	50	Ethylene glycol	Fe_3O_4	100-400	58-76.9	Polyacids[b]	39
	$FeCl_3$	200	15	Ethylene glycol	Fe_3O_4	100	63	PEG-20000	40
	$FeCl_3$	160	60	Ethylene glycol	Fe_3O_4	15	37.1	N.R.	7
	$Fe(CO)_5$	200	20	2-propyl alcohol	γ-Fe_2O_3	20	62	N.R.	41

Halloysite Nanotubes (HNT)



Halloysite Nanotubes (HNT)

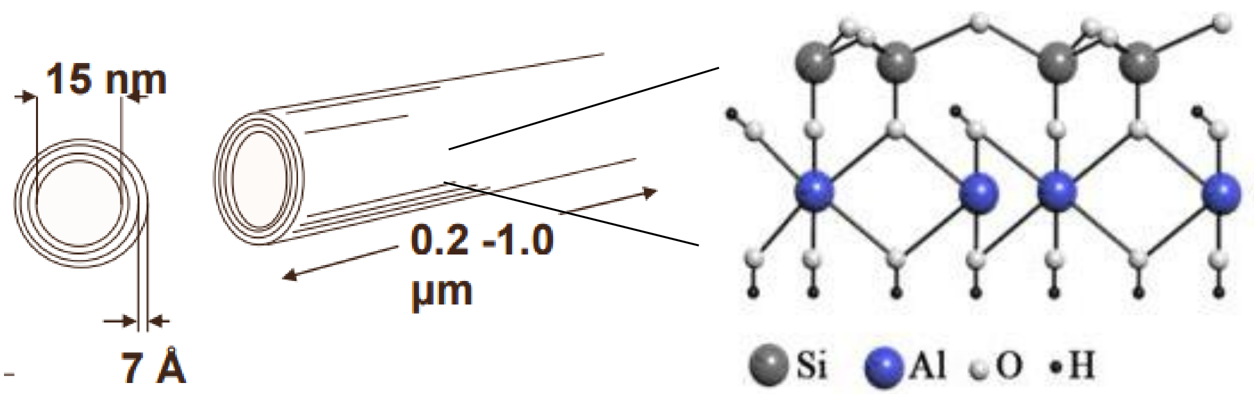


Naturally occurring aluminosilicate with ordered nanostructure which possess a characteristic hollow tubular configuration

Similar to kaolinite except for the presence of an additional water monolayer between the adjacent layers.

It forms by kaolinite layer rolling due to the action of hydrothermal processes.

$Al_2Si_2O_5(OH)_4 .2H_2O$



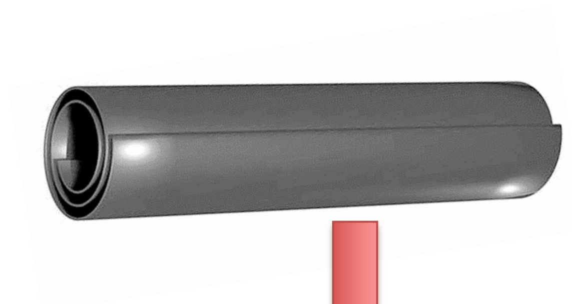
- ✓ Biocompatibility
- ✓ Empty lumen

Applications of HNT

Active agents

- **Drugs**
- **Flame retardant**
- **Antibacterials**
- **Antioxidants**

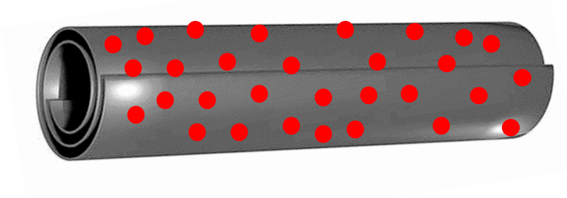
Empty lumen as confined carrier



Controlled delivering in many applications

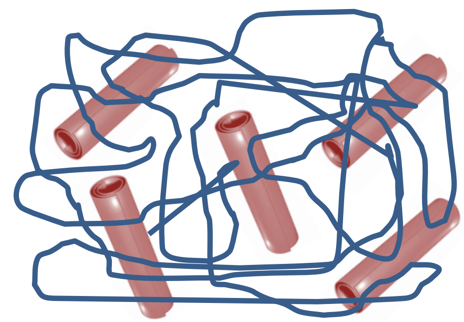
Paints
Coatings
Cosmetic
Food additives
Fragance

- Metal Nanoparticles



Catalytic supports

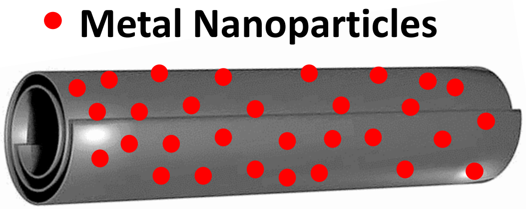
Low cost materials



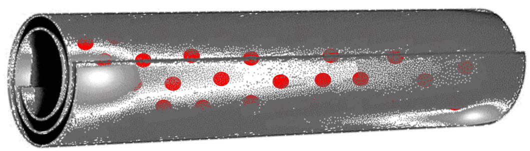
Composite: Polymer reinforce, filler, etc.

A. Spepi et al (2016) Experimental and DFT Characterization of Halloysite Nanotubes Loaded with Salicylic Acid, **Journal of Physical Chemistry-C**

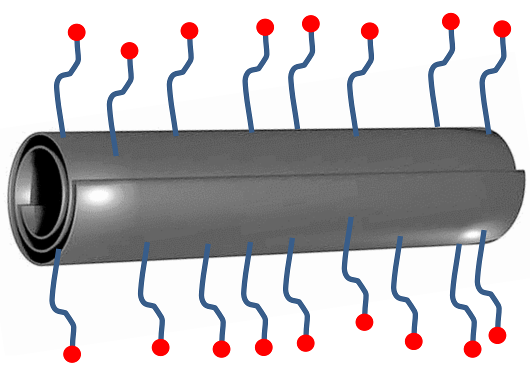
Metal Nanoparticles on HNT



On the external surface



On the internal surface



Internal/external Functionalization to covalent anchored

The location of the NPS is strongly linked to the final applications.

Carriers → functionalize the external surface

Catalysis → functionalize the internal surface

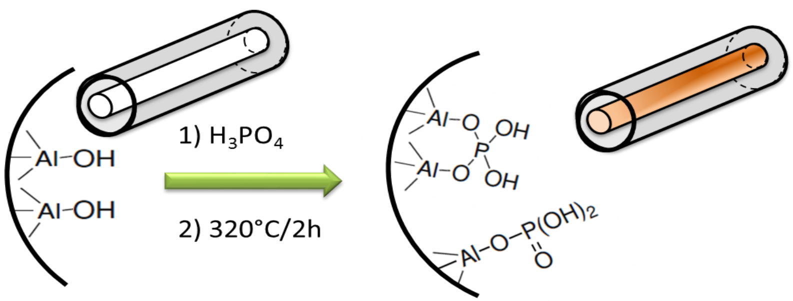
- Particular Attention on Magnetic NPs
  - Easy recovery and reuse
  - Bifunctional Materials

Methodologies to produce the composite materials must to be carefully designed

Halloysite Nanotubes grafted with iron magnetic iron oxide NPs by MW solvothermal process

Step 1. Functionalization with phosphoric acid

$$Al_2(OH)_4Si_2O_5.2H_2O\ (HNT) + H_3PO_4 \rightarrow H_2PO_4Al\text{-}(PO_4\text{-}HNT)$$



Step 2. In-situ homogeneous precipitation of iron salt precursor using urea as hydrolysis agent in a MW assisted solvothermal process

A fast urea hydrolysis:

i) the thermolysis

ii) the catalytic reaction with the phosphoric acid active sites anchored in the mesopores of HNT

1) $H_2PO_4Al\text{-} + NH_2CONH_2 + H_2O \rightarrow NH_4PO_4Al\text{-} + NH_4HPO_4Al\text{-} + CO_2 \rightarrow 2\ NH_3\ (H_2O) + HPO_4Al\text{-}$

2) $FeCl_2 + NH_4OH \rightarrow Fe(OH)_2 \rightarrow FeOOH \rightarrow Fe_3O_4$ (Fe-HNT)

MW Assisted Solvothermal Process

Solvent: Ethylene Glycol/water (2:1 v/v)
P_o=6 bar Ar, P_f=8.3 bar, T_{rxn}=175°C,
t_{rxn}=30min Power=50 W MW

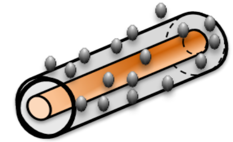
Microwave assisted High pressure reactor

Direct solvothermal deposition

MW solvothermal

(1) $FeCl_2.4H_2O$ +Urea

HNT-FeN1



Fe_3O_4 Outside

Vacuum loading/Drying/solvothermal deposition

MW solvothermal

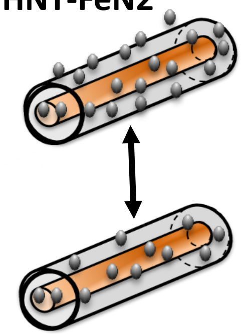
(2) $FeCl_2.4H_2O$ +Urea

Pulling and breaking vacuum process

Drying 40 °C

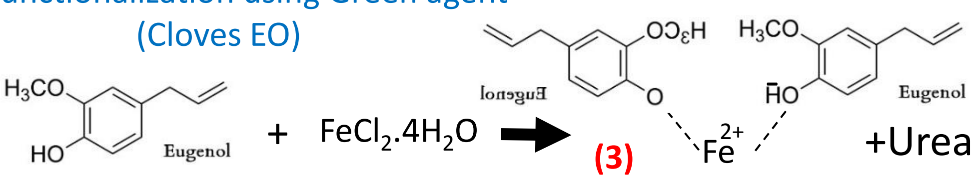
washing

HNT-FeN2



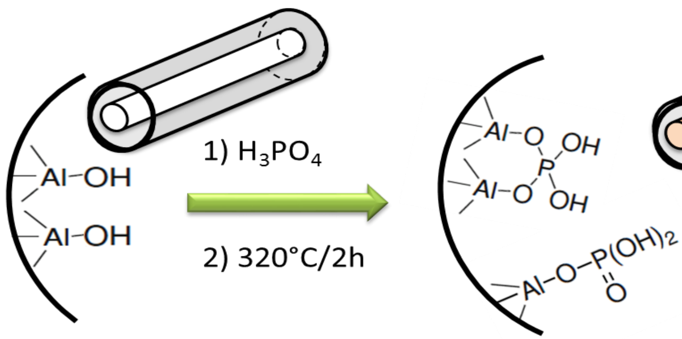
Fe_3O_4 Inside/Outside

Pre-functionalization using Green agent (Cloves EO)



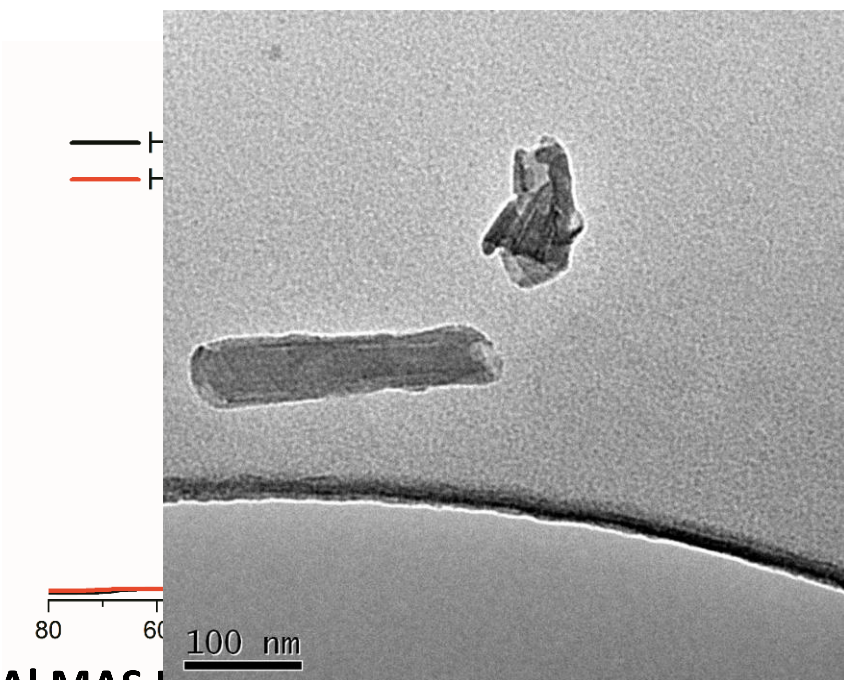
Washing with:
i) Water/etanol
ii) Hexane (dissolves the eugenol/iron complex while urea is insoluble and the external Surface of HNT is strongly hydrophilic) This process promotes a selective cleaning of the free iron on solution, outside the hollow and on the external Surface of HNT)

Selective functionalization of internal Surface

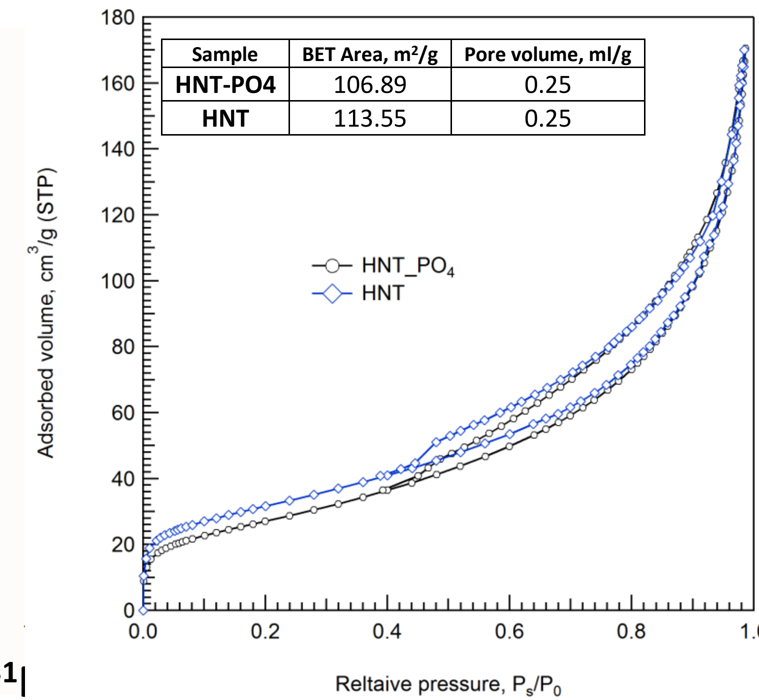


- **Binding of aluminol groups with phosporic acid**

$Al_2(OH)_4Si_2O_5.nH_2O$ (HNT) + H_3PO_4 → H_2PO_4Al-(PO_4-HNT)

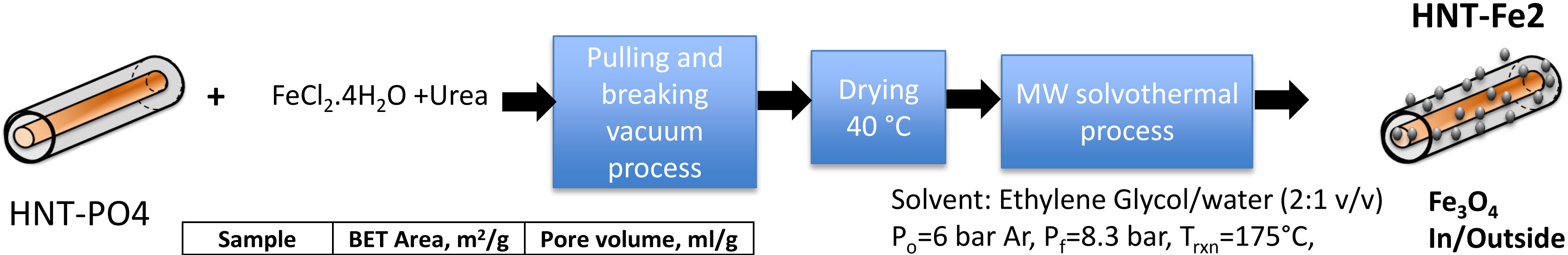


27Al MAS NMR



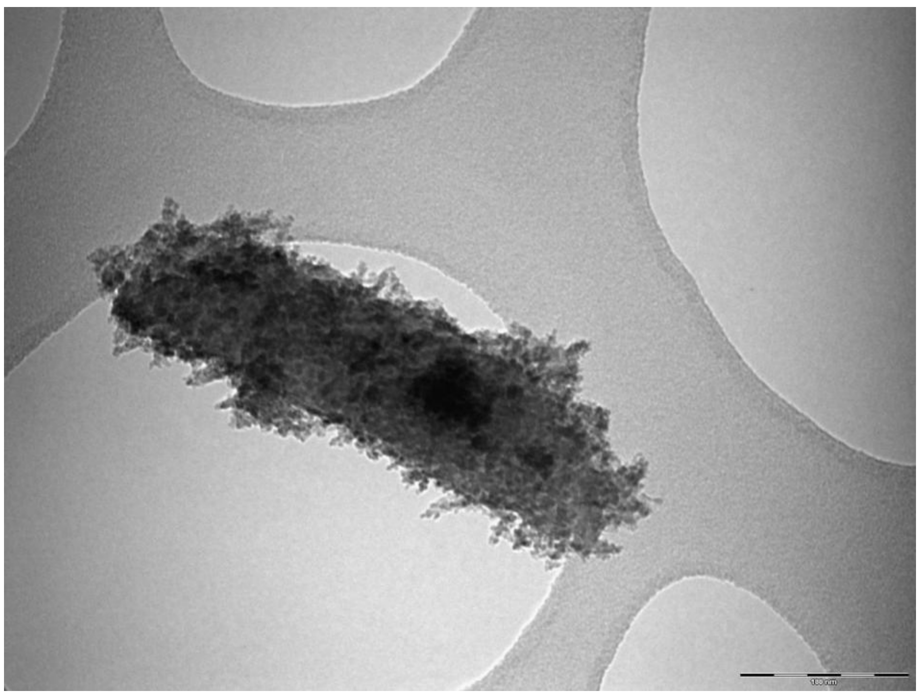
Sample	BET Area, m²/g	Pore volume, ml/g
HNT-PO4	106.89	0.25
HNT	113.55	0.25

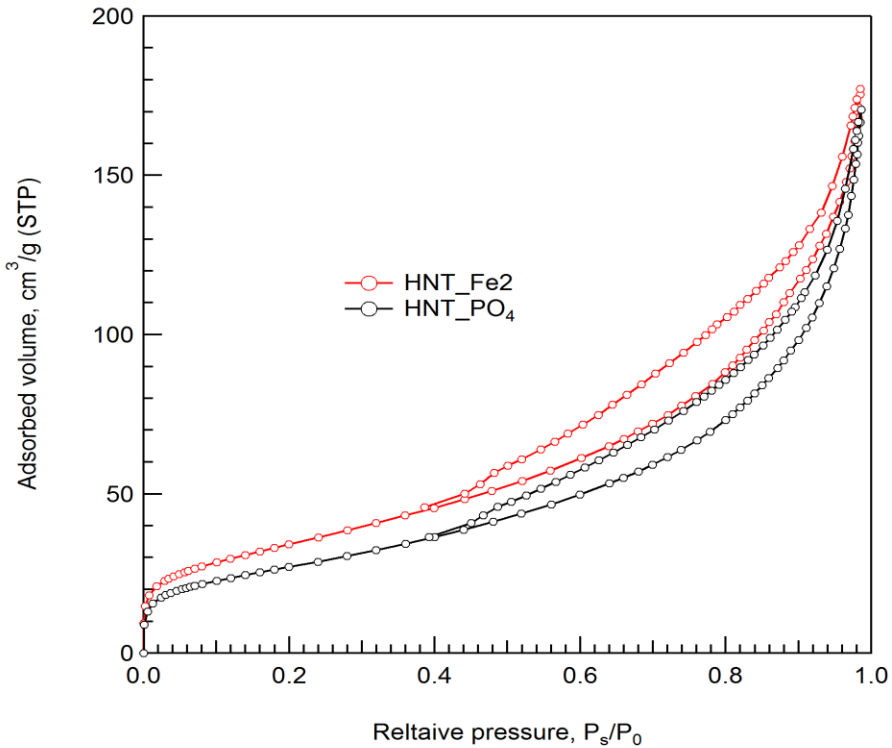
Vaccum loading/Drying/MW Solvothermal deposition



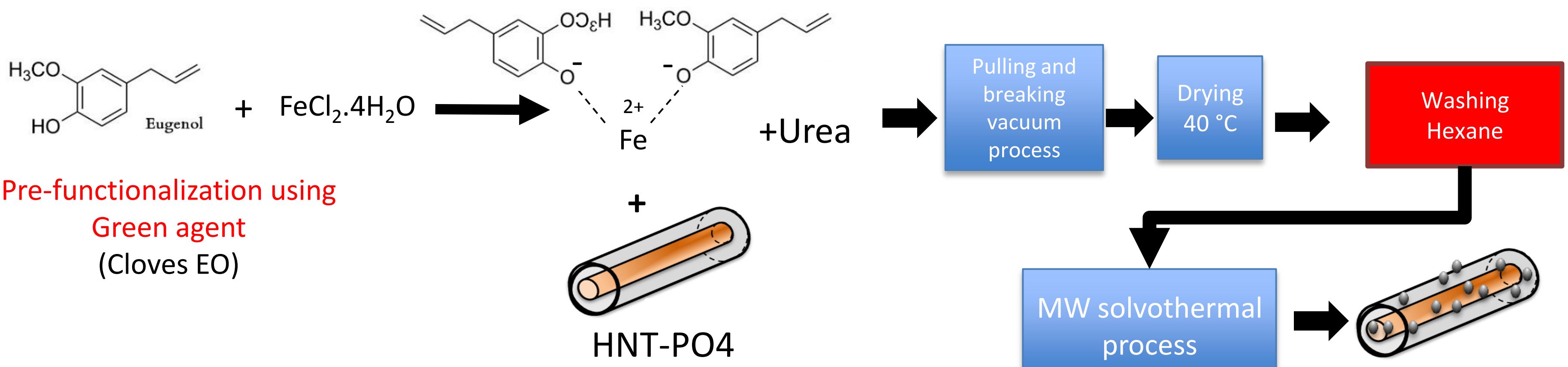
Solvent: Ethylene Glycol/water (2:1 v/v)
P_o=6 bar Ar, P_f=8.3 bar, T_{rxn}=175°C,
t_{rxn}=30min Power=50 W MW

Sample	BET Area, m²/g	Pore volume, ml/g
HNT-PO4	106.89	0.25
HNT-Fe2	124.11	0.25





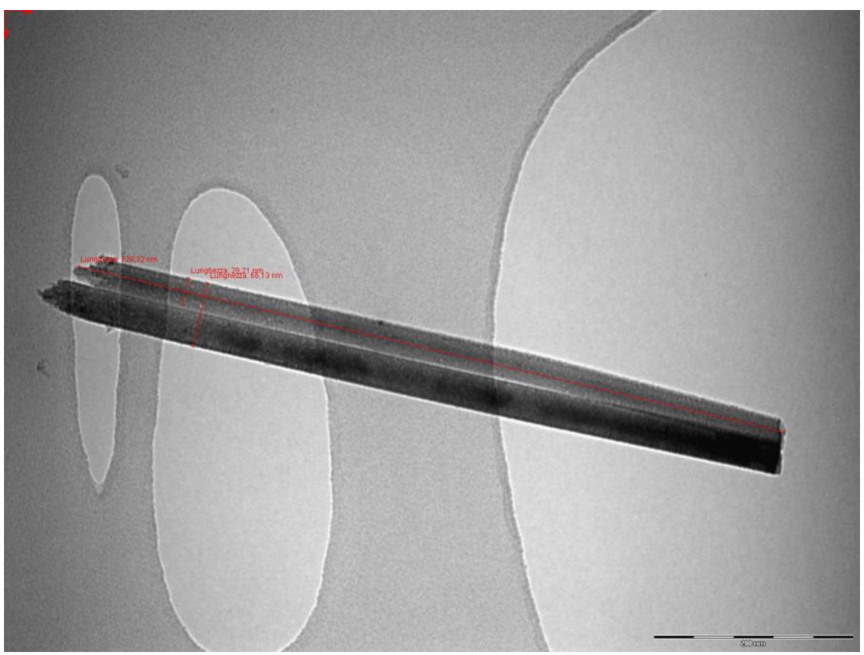
Vaccum loading/Drying/MW Solvothermal deposition

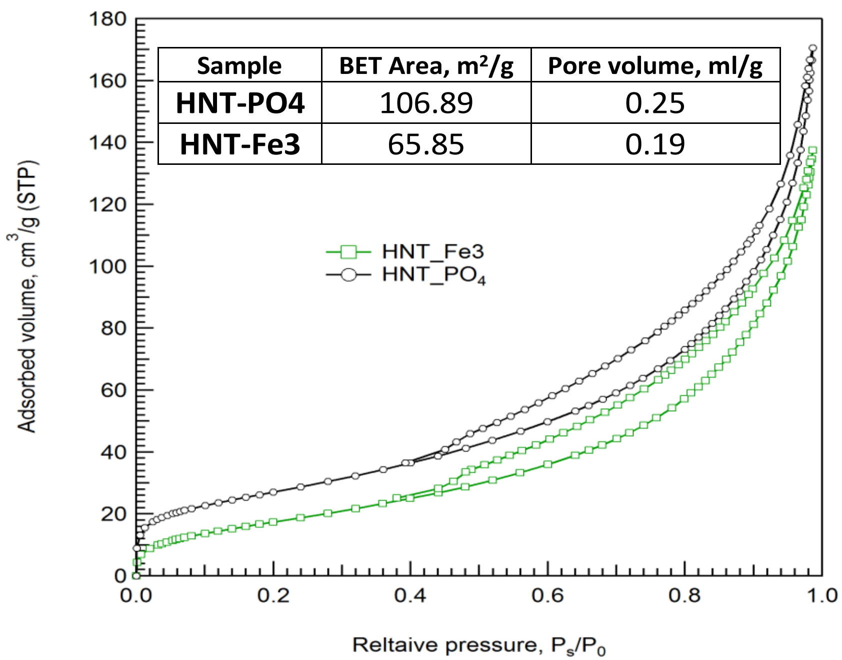


Pre-functionalization using Green agent (Cloves EO)

Solvent: Ethylene Glycol/water (2:1 v/v)
P_o=6 bar Ar, P_f=8.3 bar, T_{rxn}=175°C,

HNT-Fe3





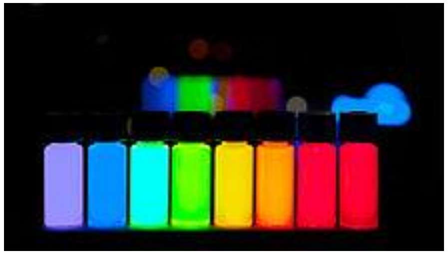
Sample	BET Area, m²/g	Pore volume, ml/g
HNT-PO4	106.89	0.25
HNT-Fe3	65.85	0.19

Fluorescent Silicon Nanoparticles synthesis by Microwave assisted process

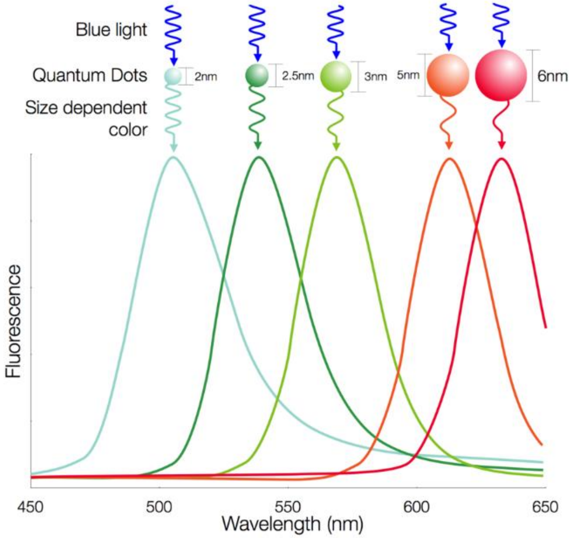
Quantum dots

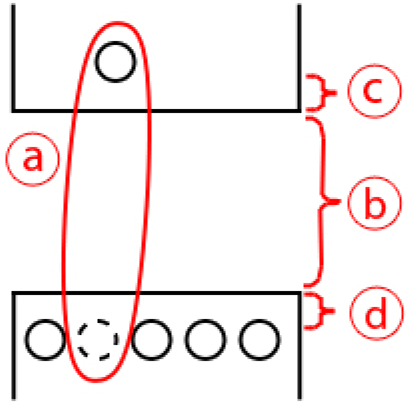
- Crystal of semiconductor material whose diameter is on the order of several nanometers (between 2 and 10 nanometers) a size which results in its free charge carriers experiencing "quantum confinement" in all three spatial dimensions.
- Light absorption generally leads to an electron being excited from the valence to the conduction band, leaving behind a hole. The electron and the hole can bind to each other to form an exciton. When this exciton recombines (i.e. the electron resumes its ground state), the exciton's energy can be emitted as light

PbS, PbSe, CdSe, CdS, CdTe, InAs, InP



Quantum Dot Size and Color



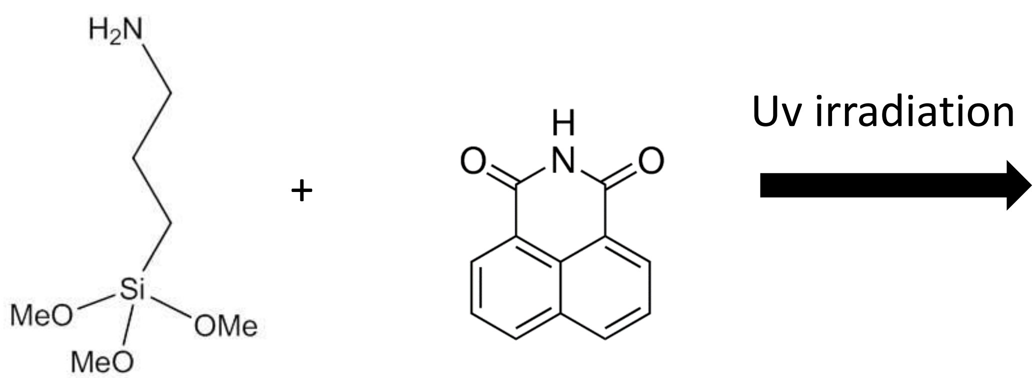


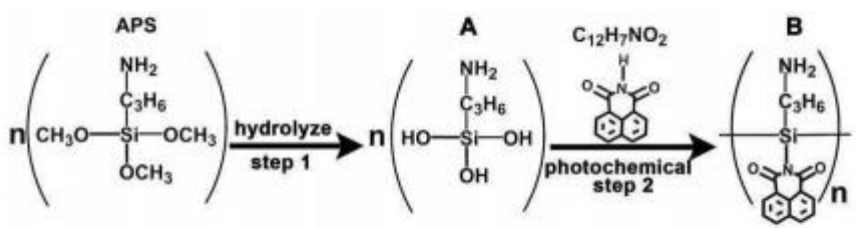
- (a) Exciton (electron-hole pair)
- (b) Band gap
- (c) Zero point vibrational energy of the excited electron
- (d) Zero point vibrational energy of the hole

Silicon based QDs

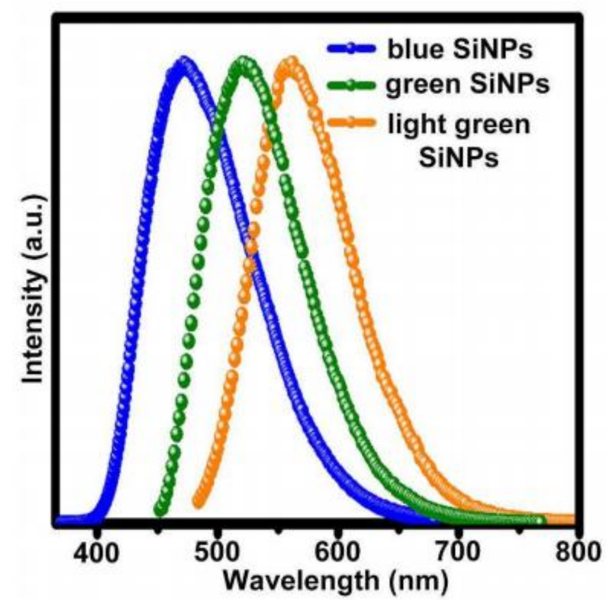
Photochemical Reduction

Zhong, X. et al (2015)*





15, 30 40 min



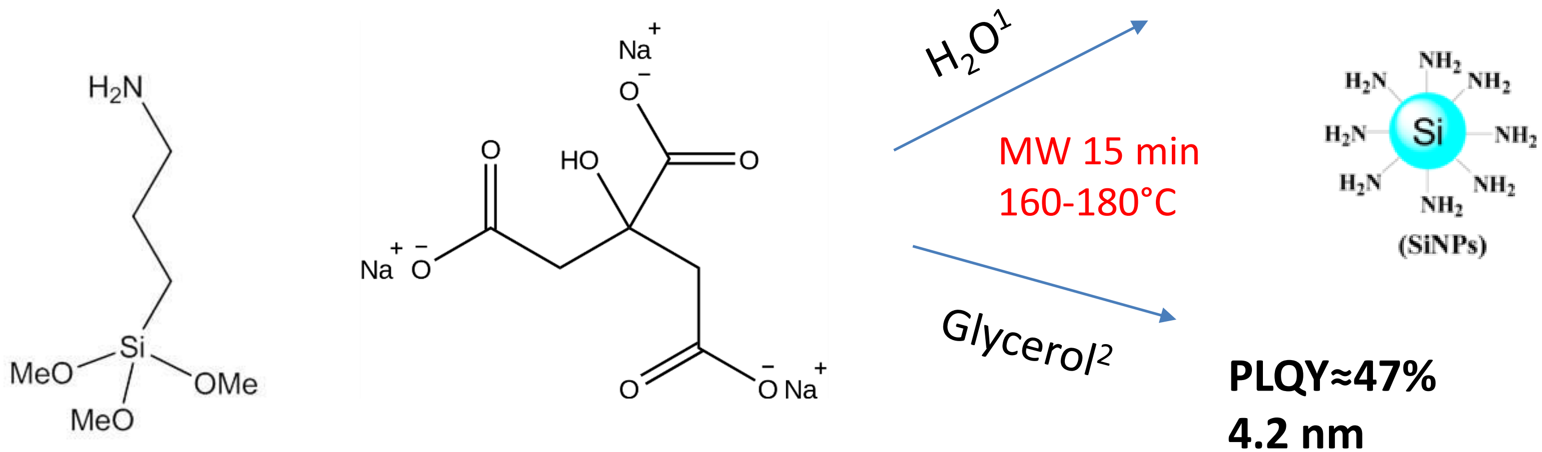
PLQY≈25%
2-4 nm

*Y. Zhong, X. Sun, S. Wang, F. Peng, F. Bao, Y. Su, Y. Li, S. T. Lee and Y. He, *ACS Nano*, 2015, **9**, 5958–5967.

MW assisted Hydrothermal Process(lit. rev.)

Hydrothermal process by Y. Zhong et al (2013)[1]
Solvothermal process by H.L. Ye et al (2016)[2]

PLQY≈20-25%
2.2 nm



[1]Y. Zhong, F. Peng, F. Bao, S. Wang, X. Ji, L. Yang, Y. Su, S.-T. Lee and Y. He, *J. Am. Chem. Soc.*, 2013, **135**, 8350–8356.
[2]H.-L. Ye, S.-J. Cai, S. Li, X.-W. He, W.-Y. Li, Y.-H. Li and Y.-K. Zhang, *Anal. Chem.*, 2016, **88**, 11631–11638.

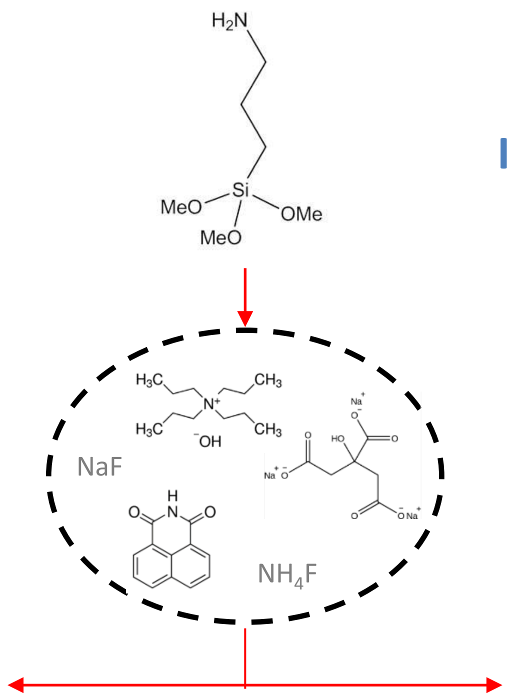
Improve MW assisted processes using a coaxial configuration (our approach)

Simultaneous MW-UV irradiation

Coaxial antenna (I), reflux system (II), glass reactor (III), N2 inlet (IV) and stirrer (V).

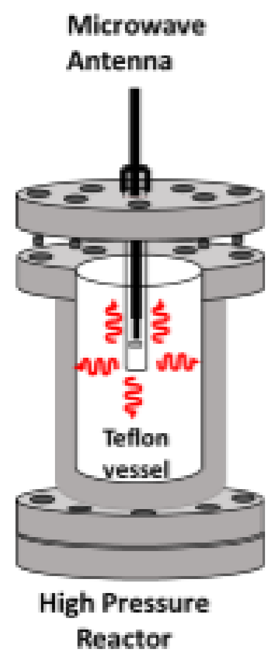
Synthesis reactors

Silicon precursor



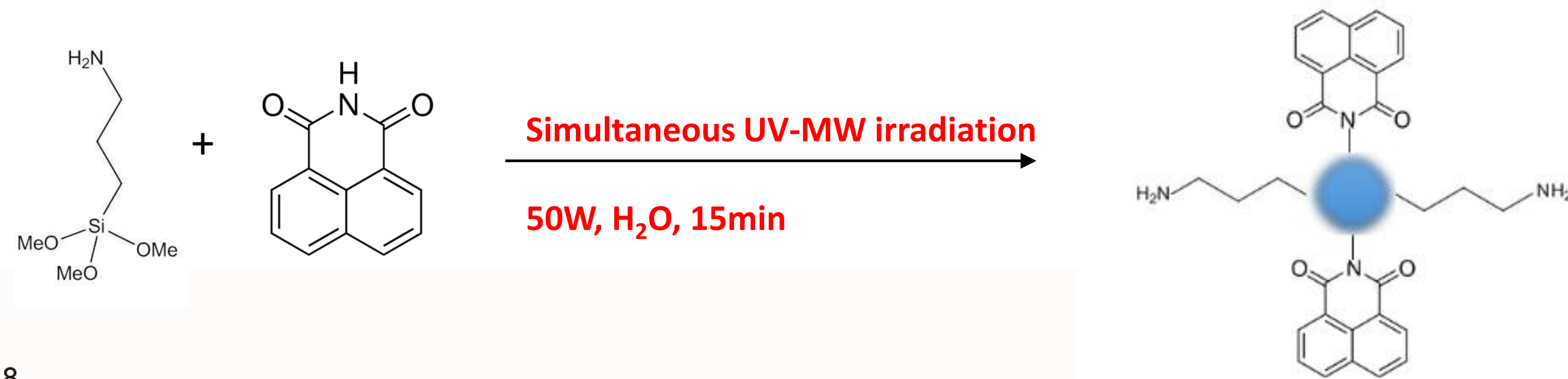
Different reducing agents and the incorporation of structure directing agents to promote microporosity

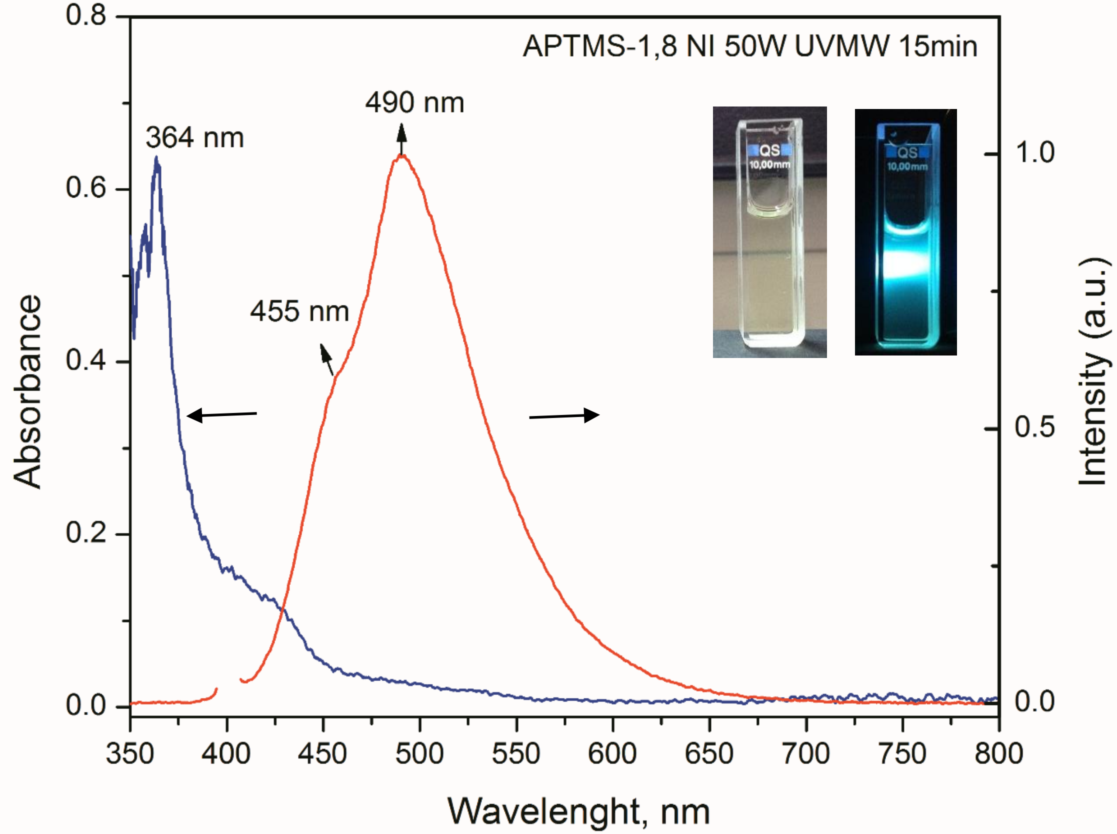
In-situ MW irradiation (non oven approach)



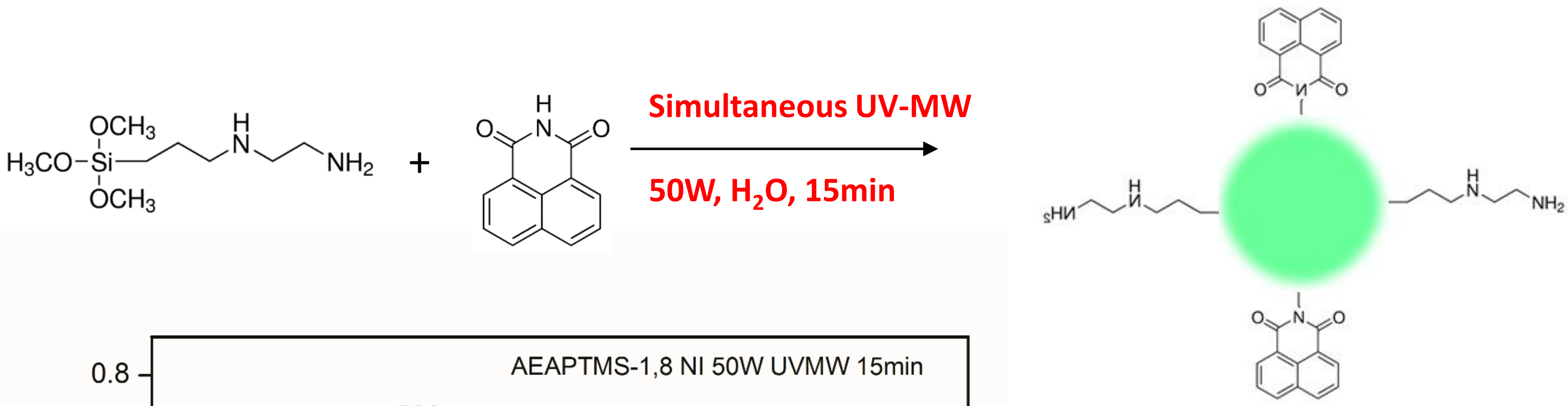
Solvothermal reactors

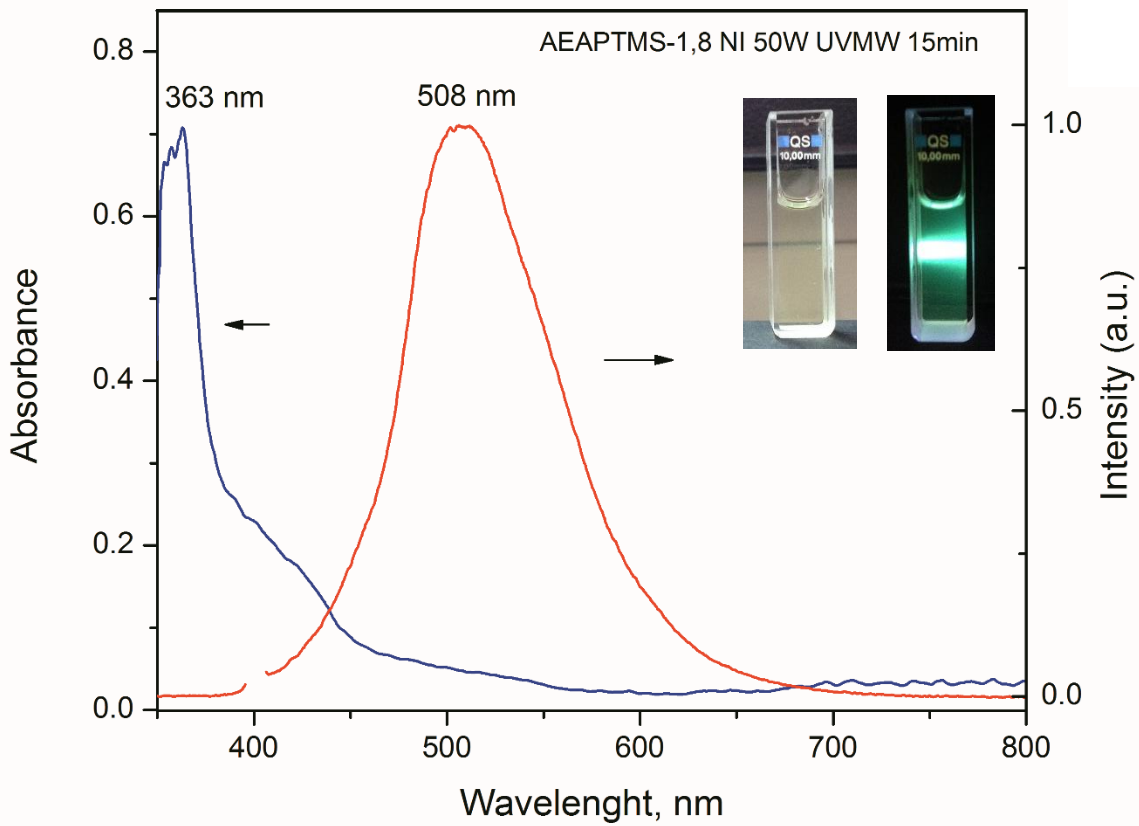
Simultaneous UV-MW irradiation to promote APTMS photoreduction



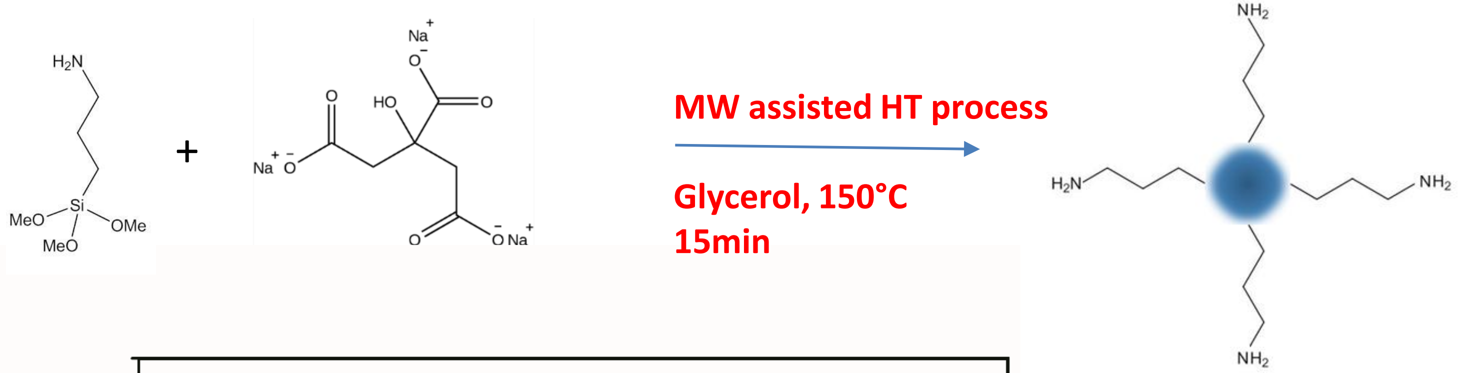


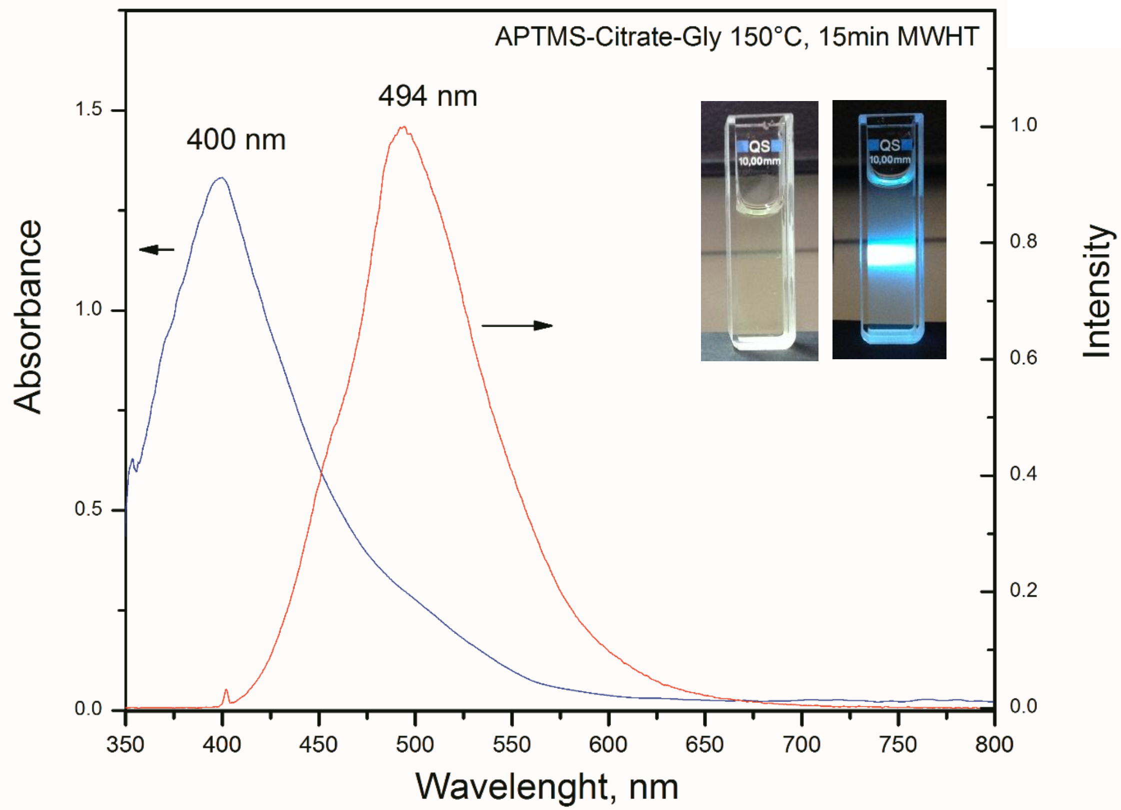
Simultaneous UV-MW irradiation to promote AEAPTMS photoreduction



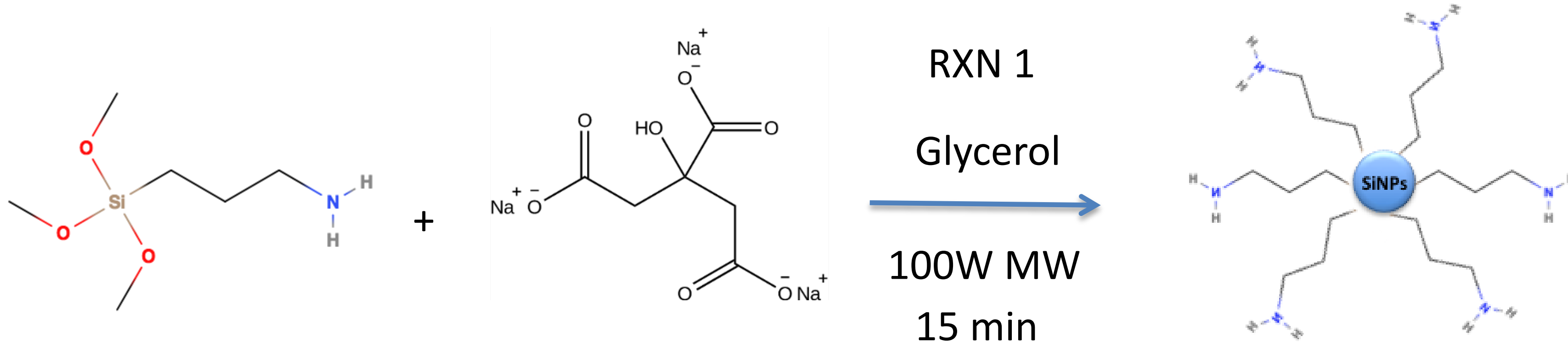


MW assisted solvothermal synthesis



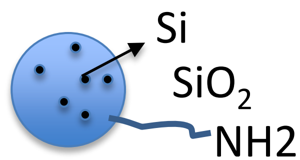


APTMS based Silicon nanoparticles

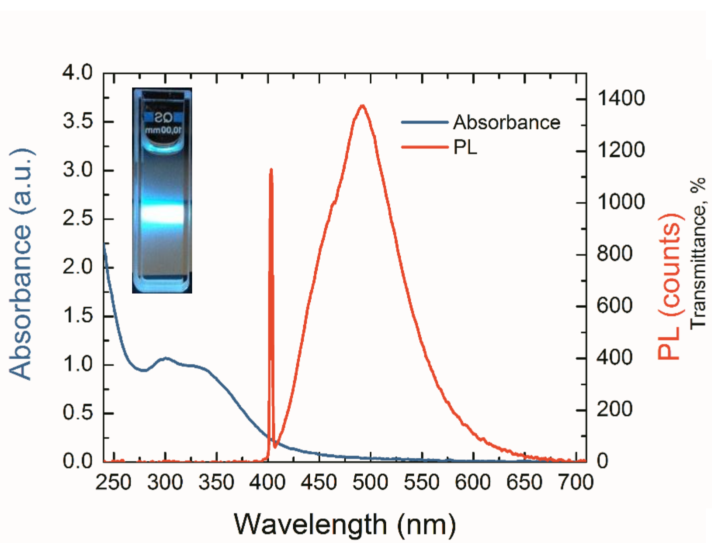


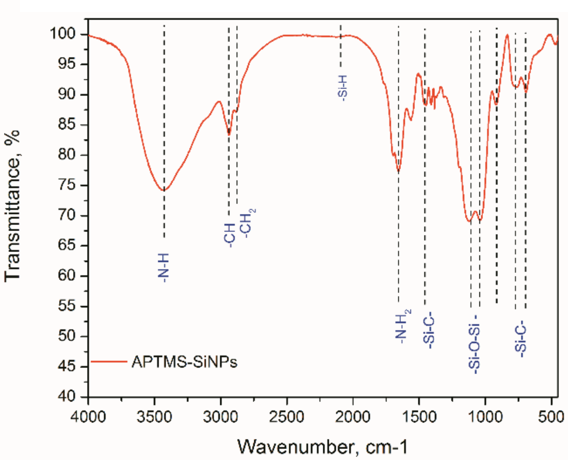
pH=10.8

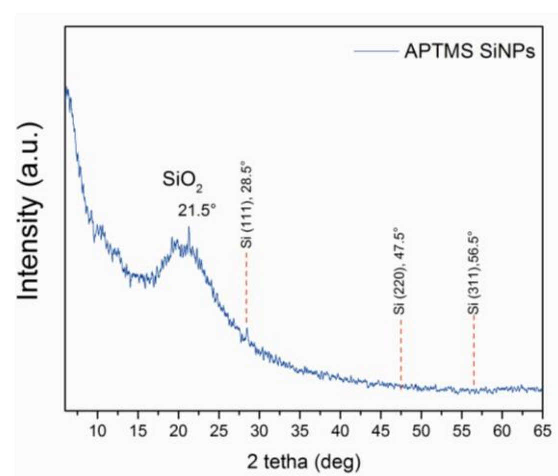
pH=10.2



- **Crystals nuclei**
- **Amorphous shell**
- **Organic surface**

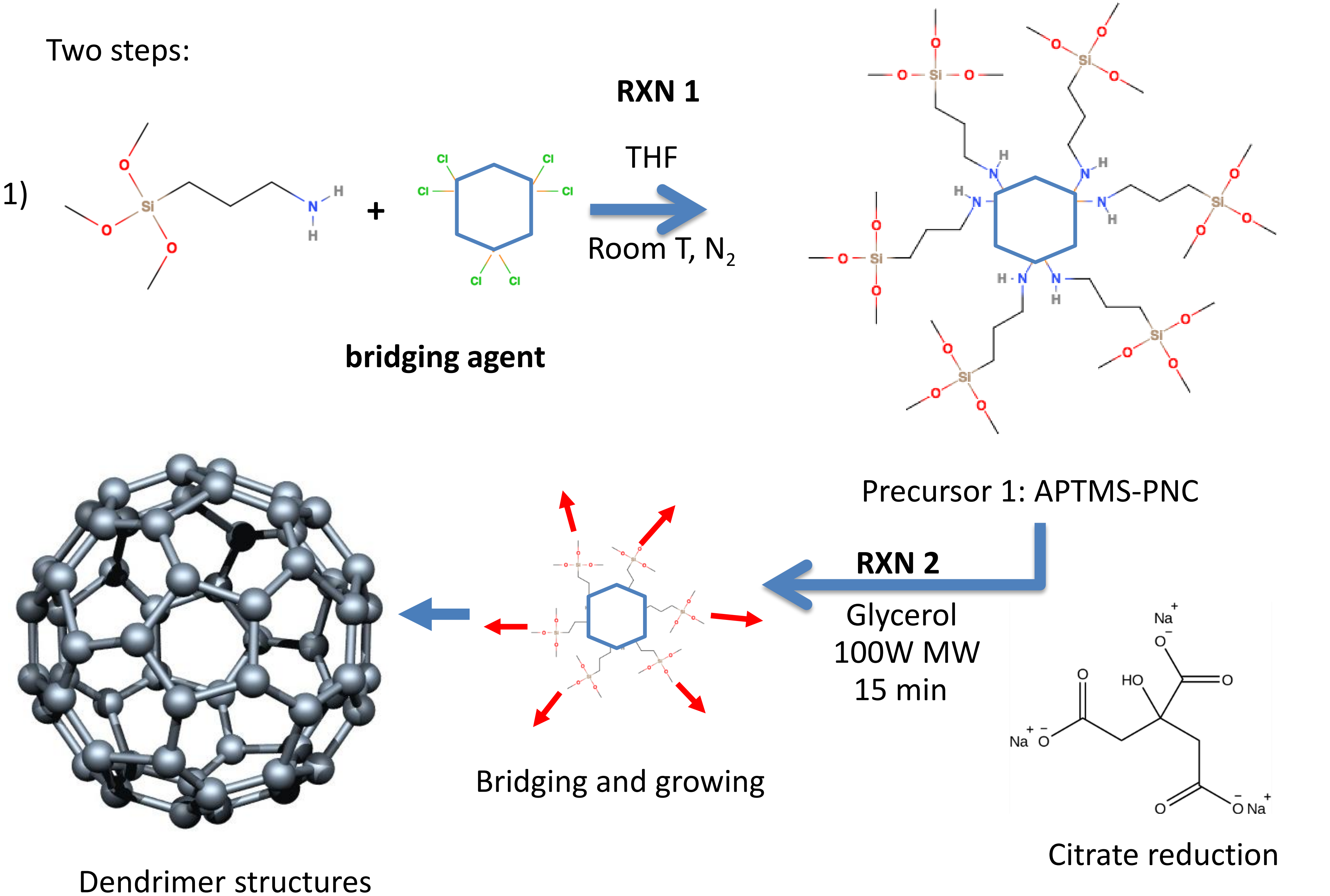




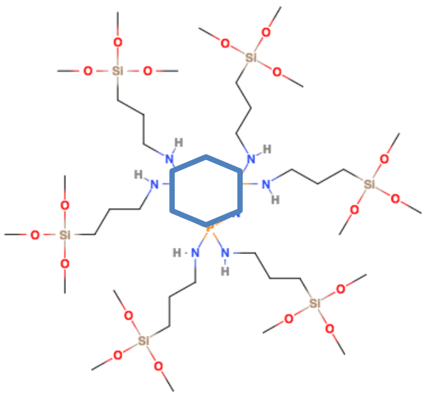


APTMS-PNC assembled Silicon nanoparticles

Exotermic reaction

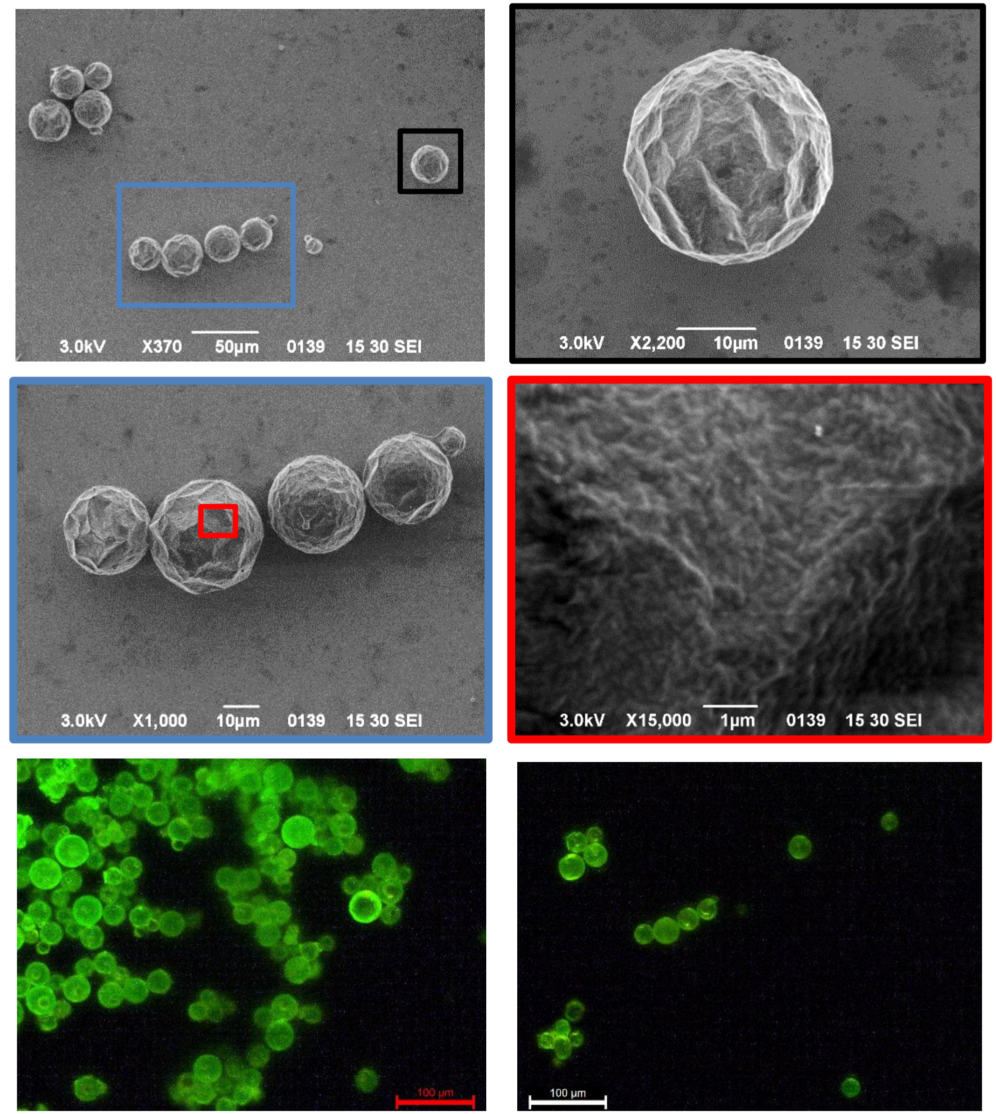


APTMS-PNC assembled Silicon nanoparticles

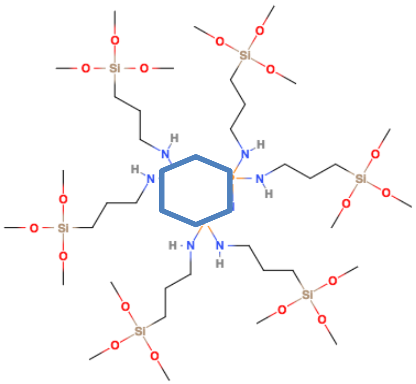


MW assisted synthesis

Glycerol
100W MW
15 min



APTMS-PNC assembled Silicon nanoparticles



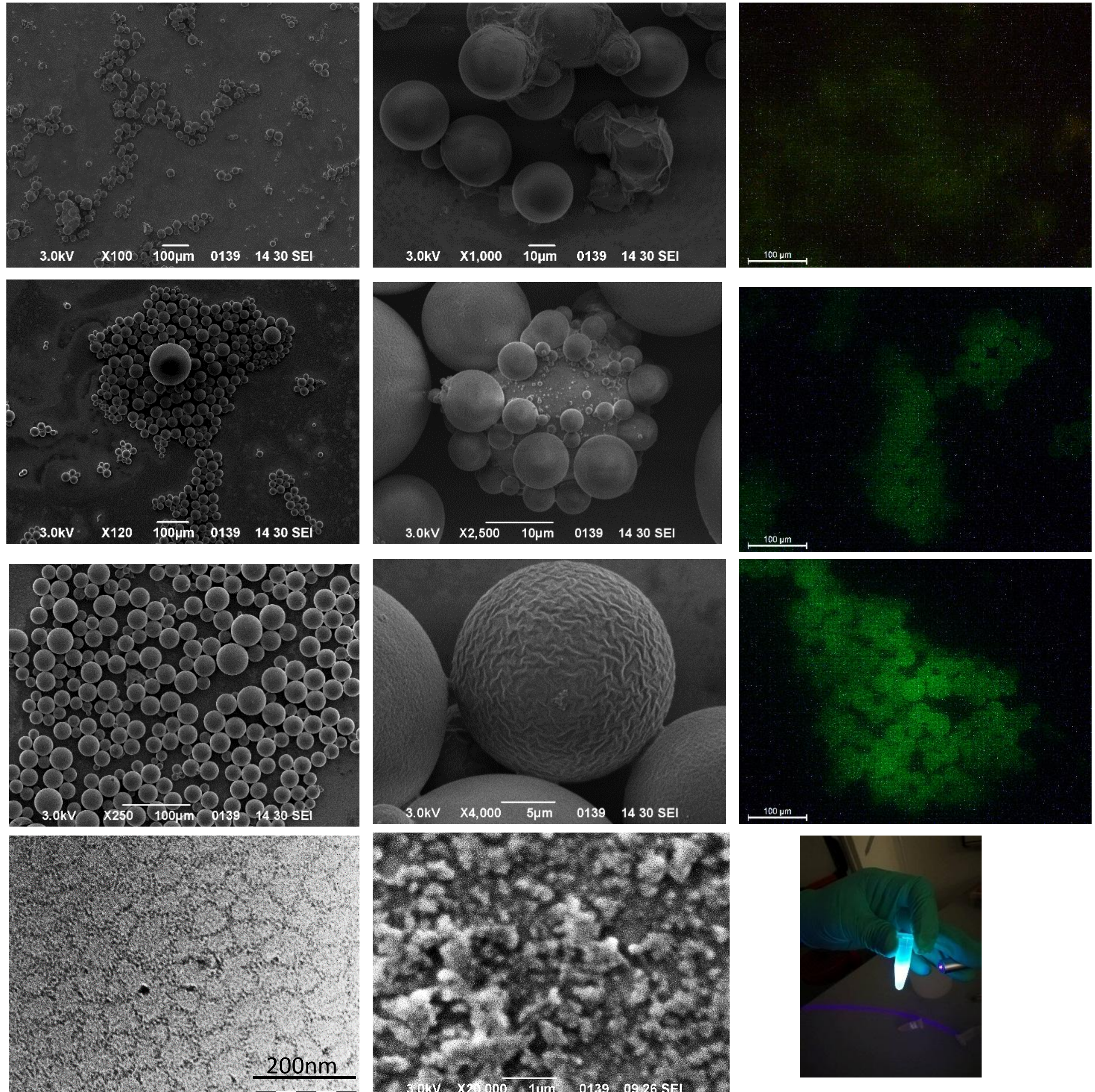
Si-PNC
6:1 mol ratio

5 min

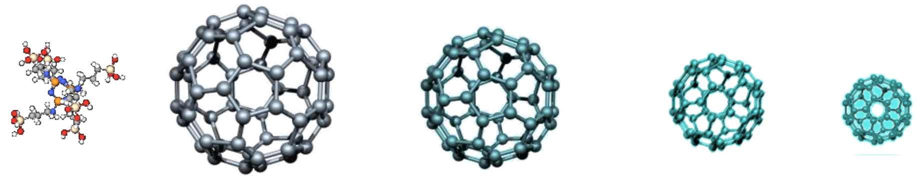
10 min

15 min

30 min



APTMS-PNC assembled Silicon nanoparticles

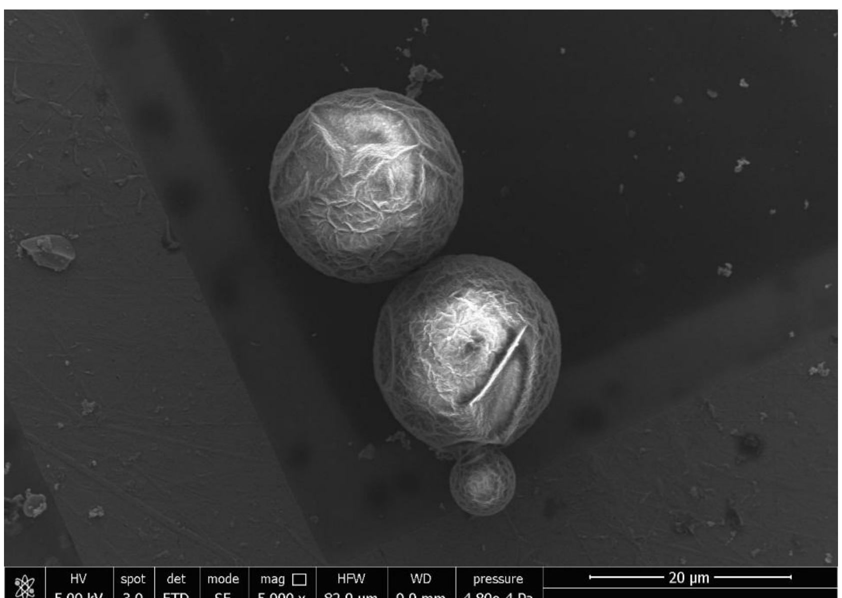


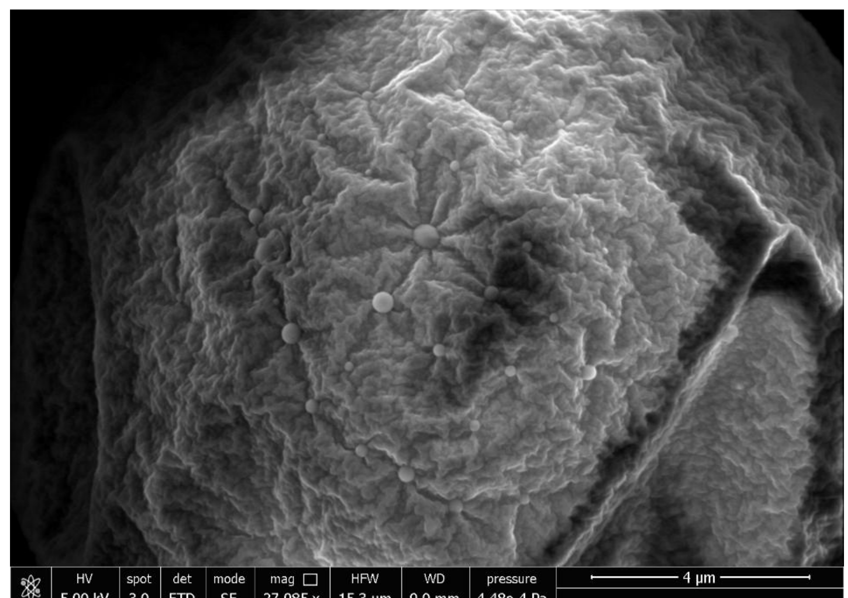
RXN conditions
Glycerol 100W MW

time	0	5	10	15	30 min
pH	6.84	4.76	3.87	3.56	2.98

Microparticles built up by smaller particles starting from single molecules….. Inverse dendrimer like formation?

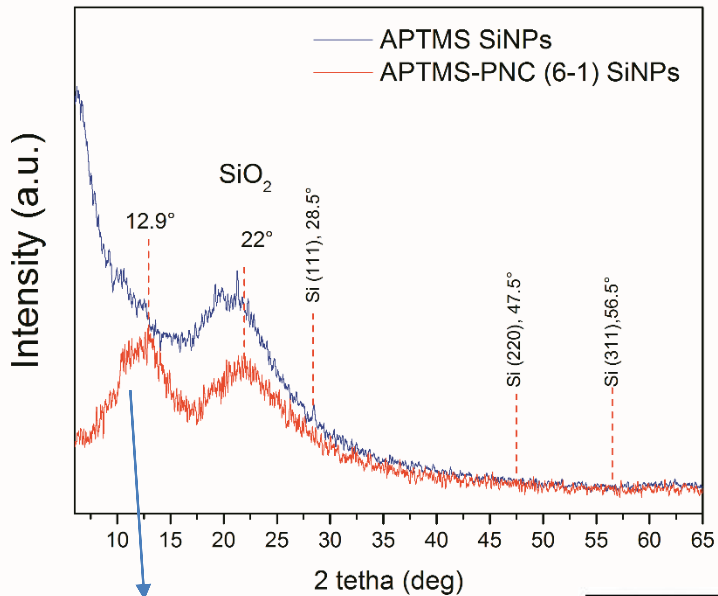
Dendrite like morphology



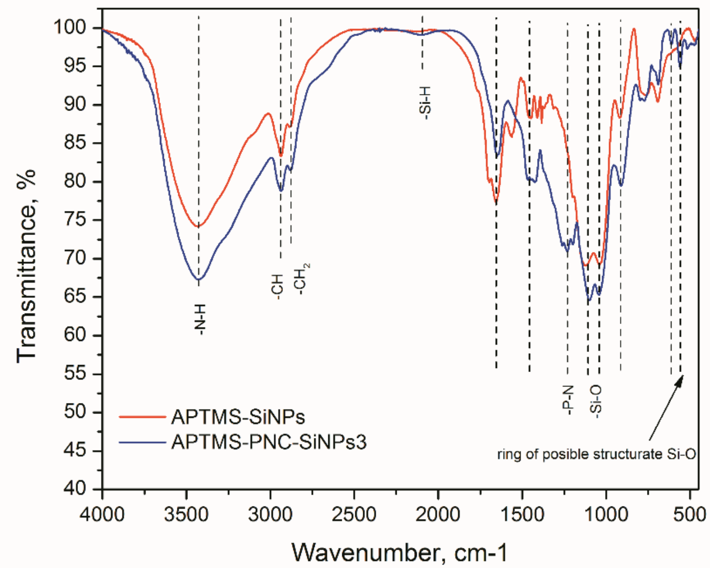


APTMS-PNC assembled Silicon nanoparticles

XRD diffraction pattern

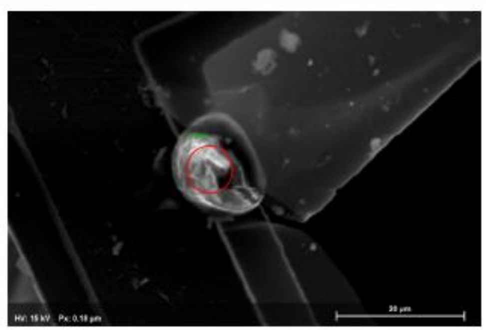


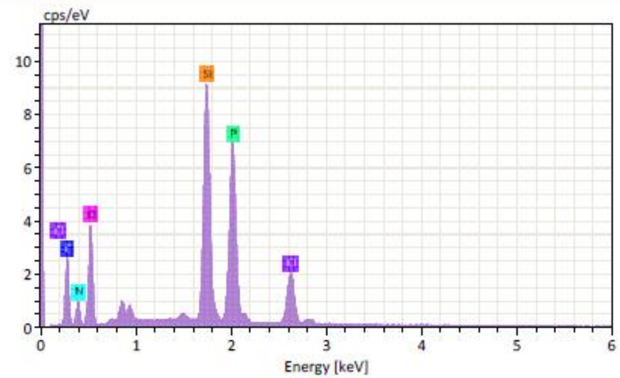
FTIR spectroscopy



Possible nanocage ?

EDS analysis



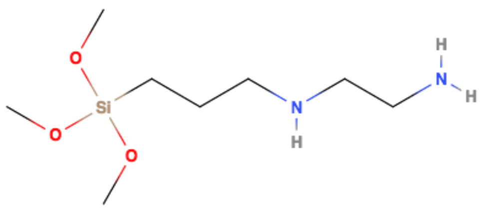


2 316

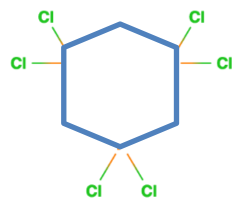
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Carbon	6	6462	22.45	27.79	38.84	3.39
Nitrogen	7	2513	10.51	13.00	15.59	1.91
Oxygen	8	11326	20.84	25.79	27.07	2.89
Silicon	14	43049	11.34	14.03	8.39	0.50
Phosphorus	15	34507	11.05	13.67	7.41	0.45
Chlorine	17	11312	4.61	5.71	2.70	0.19
		Sum	80.80	100.00	100.00	

AEAPTMS-PNC assembled Silicon nanoparticles

Different configurations



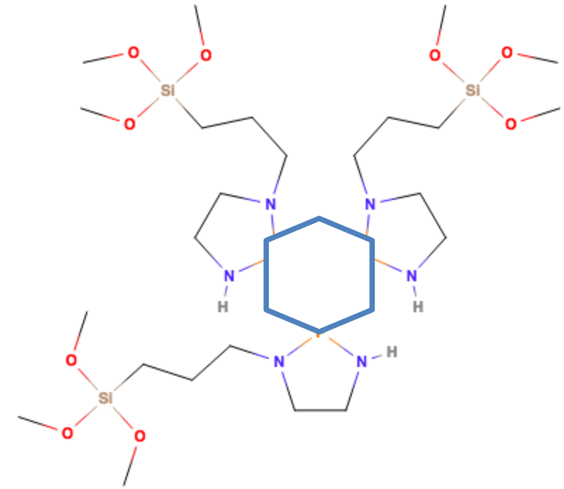
+



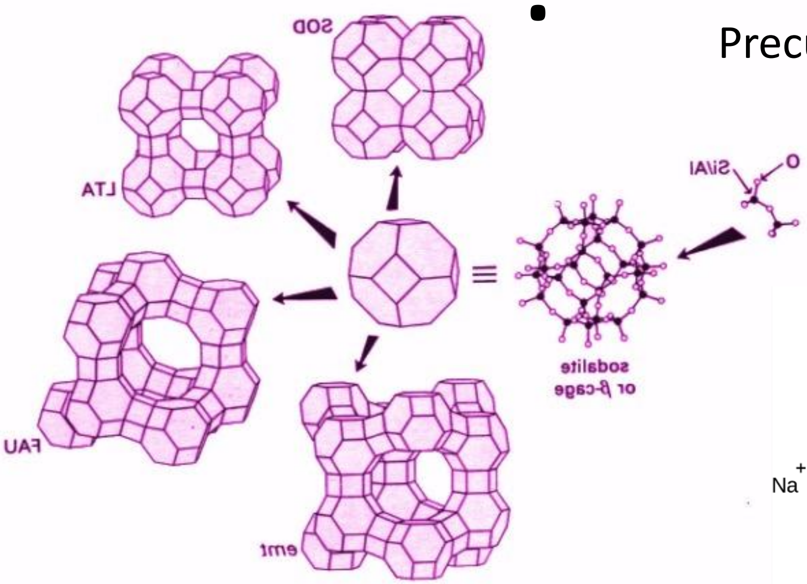
RXN 1

THF

Room T, N_2



?

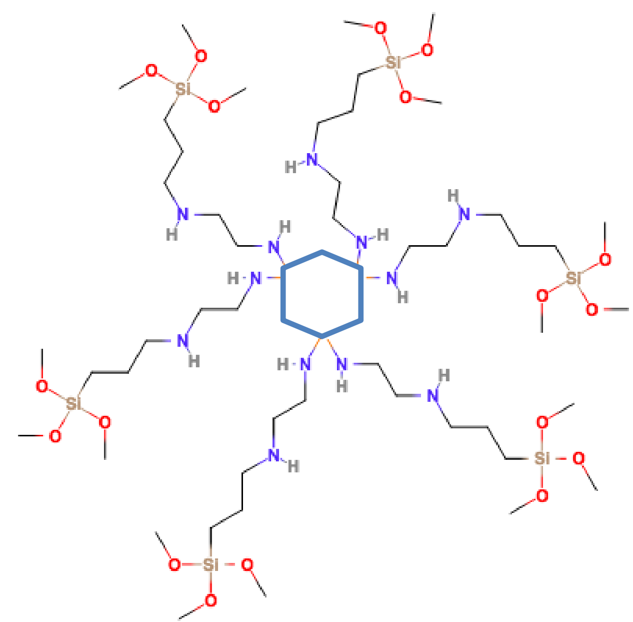


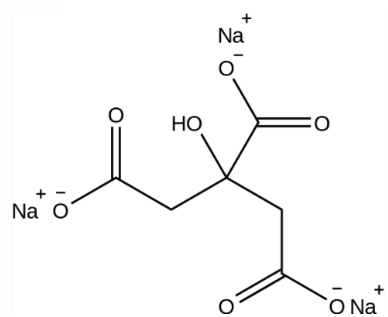
Precursor 2: AEAPTMS-

RXN 2

Glycerol 15 m

100W MW

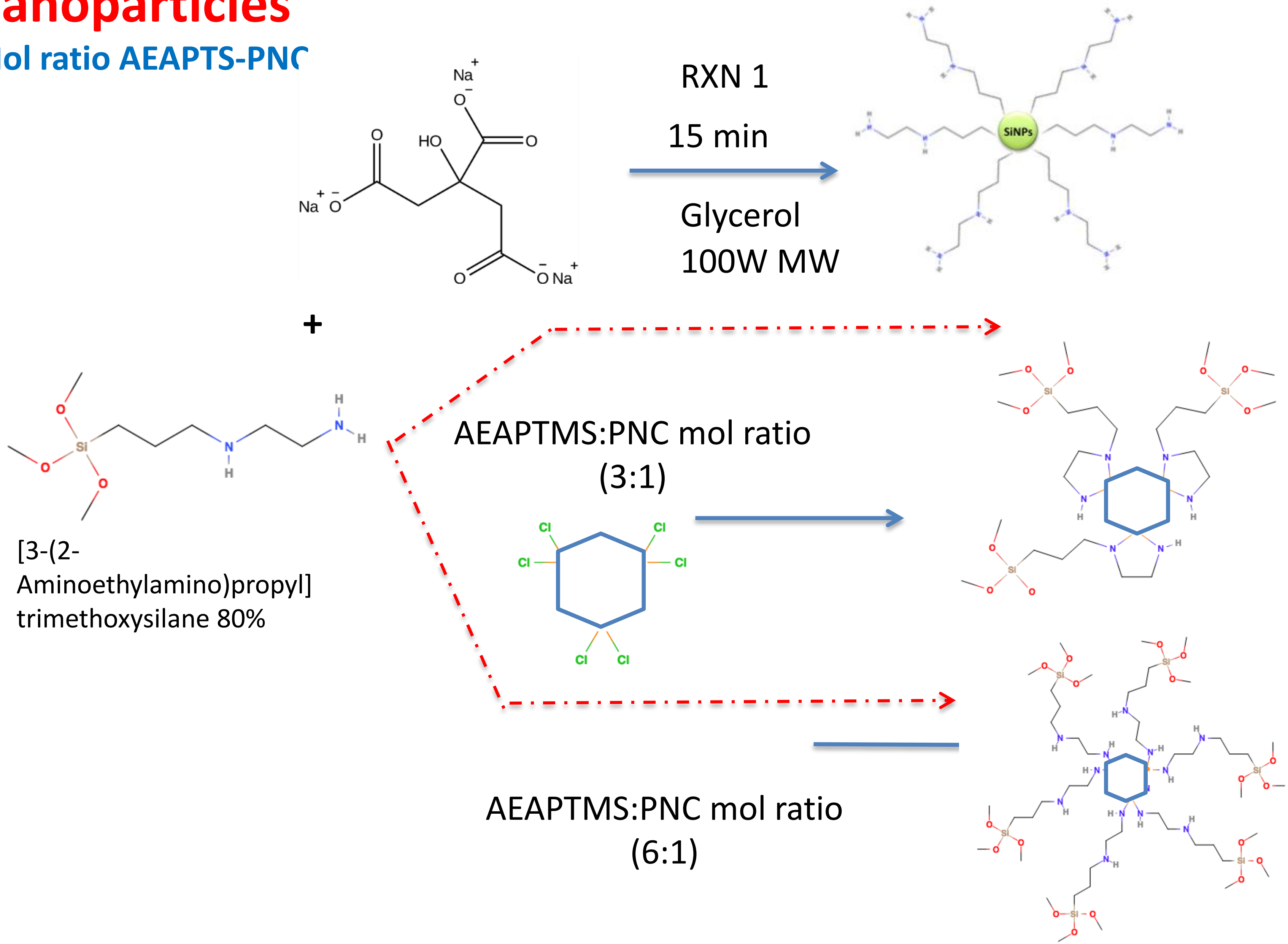




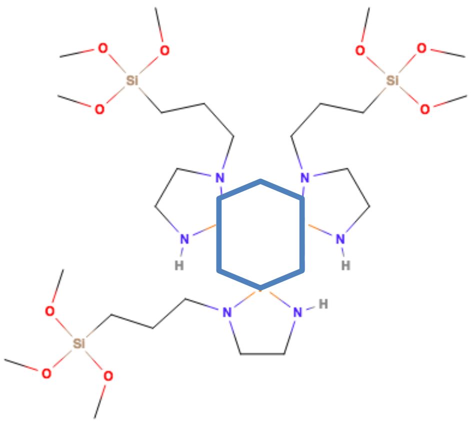
Citrate reduction

AEAPTMS-PNC assembled Silicon nanoparticles

Mol ratio AEAPTS-PNC



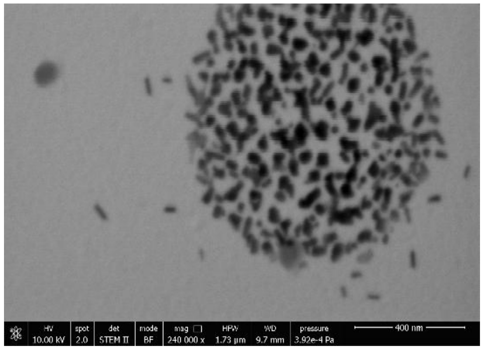
AEAPTMS-PNC assembled Silicon nanoparticles

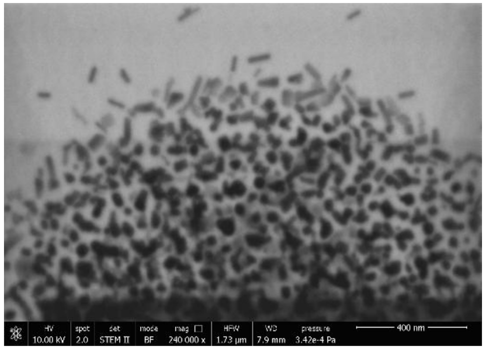


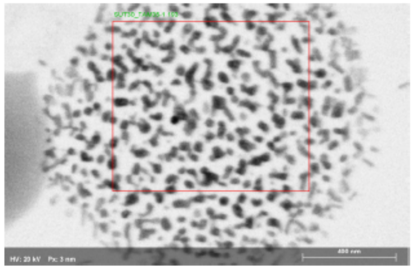
MW assisted synthesis

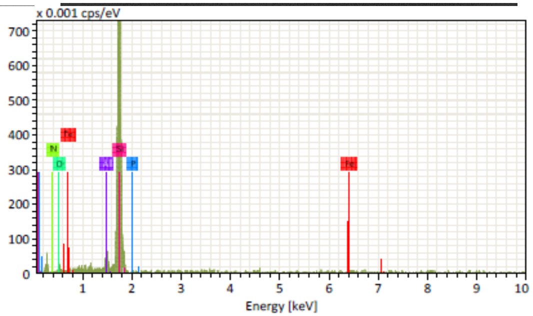
15 min

AEAPTMS:PNC mol ratio (3:1)







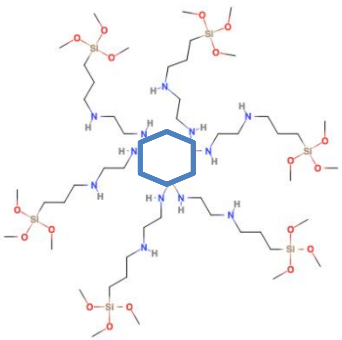


SUT30_TAM35-1 193

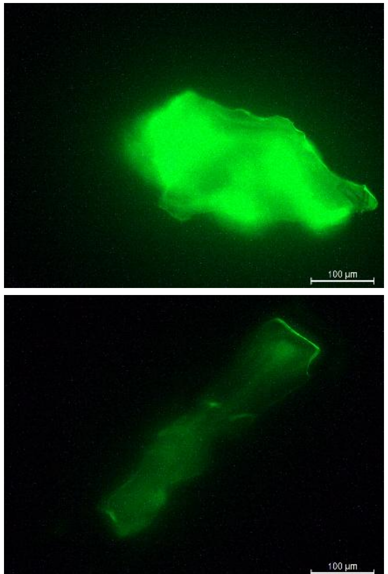
Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	abs. error [%] (2 sigma)	abs. error [%] (3 sigma)	rel. error [%] (1 sigma)	rel. error [% (2 sigma)
Nitrogen	7	K-Serie	6	0.93	1.61	3.05	1.67	3.34	5.00	179.48	358.9
Oxygen	8	K-Serie	53	3.07	5.32	8.84	2.02	4.04	6.06	65.77	131.5
Aluminium	13	K-Serie	145	1.72	2.98	2.93	0.22	0.44	0.66	12.77	25.5
Silicon	14	K-Serie	4360	51.96	90.01	85.14	2.50	5.00	7.50	4.81	9.6
Phosphorus	15	K-Serie	0	0.00	0.00	0.00	0.00	0.00	0.00	1.87	3.7
Iron	26	K-Serie	1	0.05	0.09	0.04	0.04	0.08	0.13	85.04	170.0
			Sum	57.73	100.00	100.00					

Are these NPs the Si nanocrystals?

AEAPTMS-PNC assembled Silicon nanoparticles



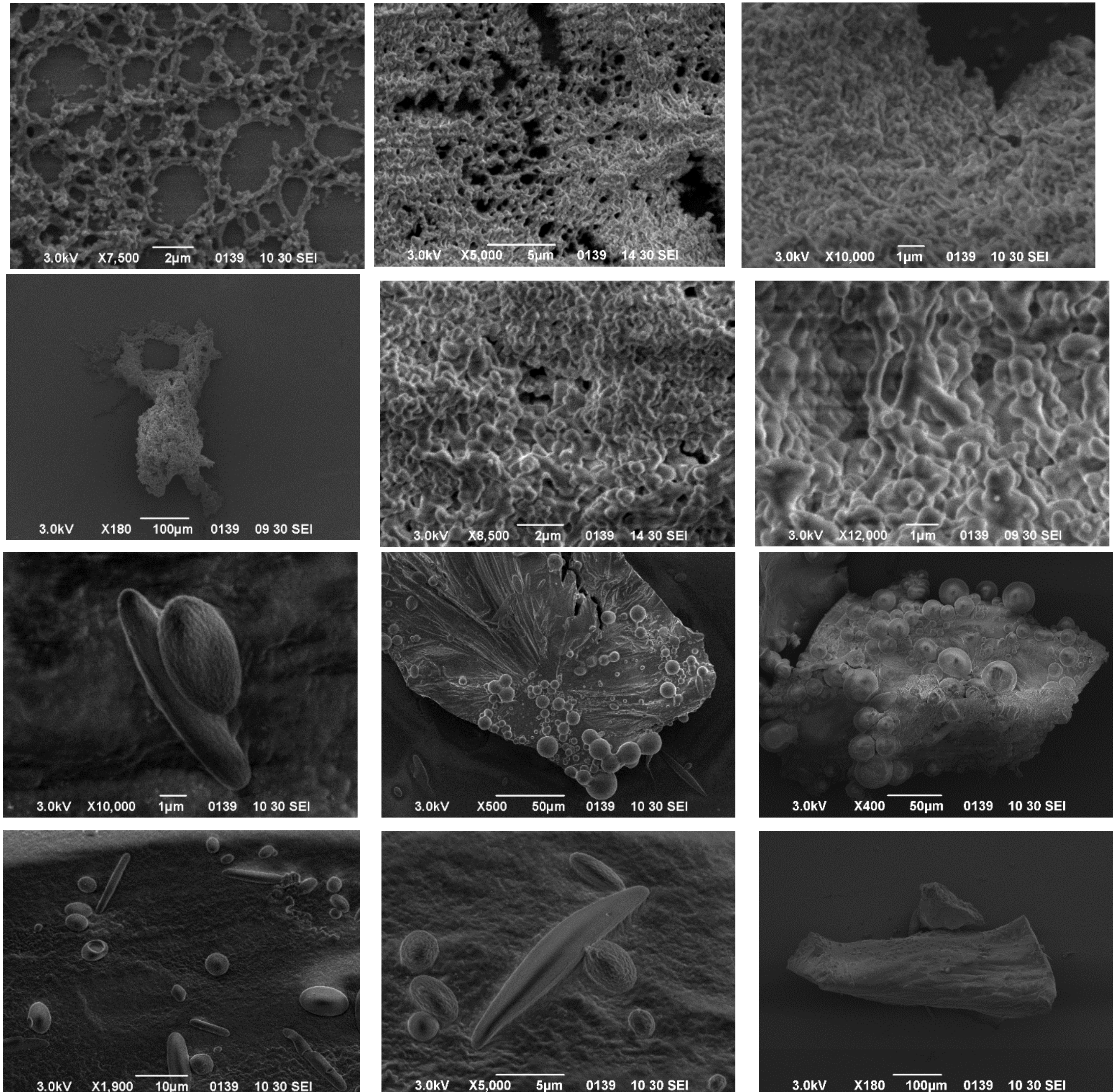
AEAPTMS:PNC mol ratio (6:1)



3 min

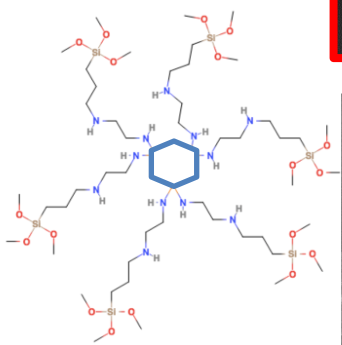
5 min

7 min

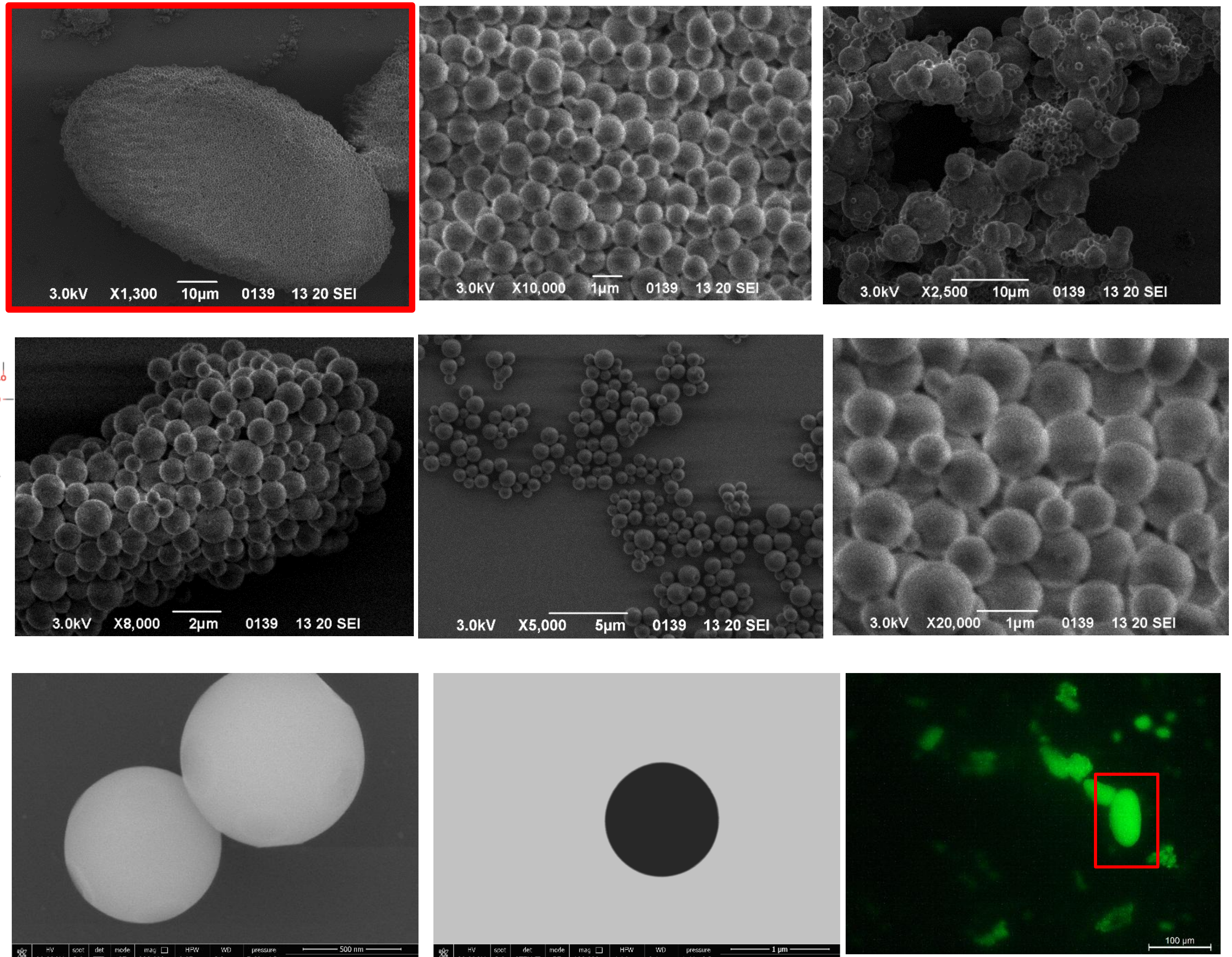


AEAPTMS-PNC assembled Silicon nanoparticles

30 min



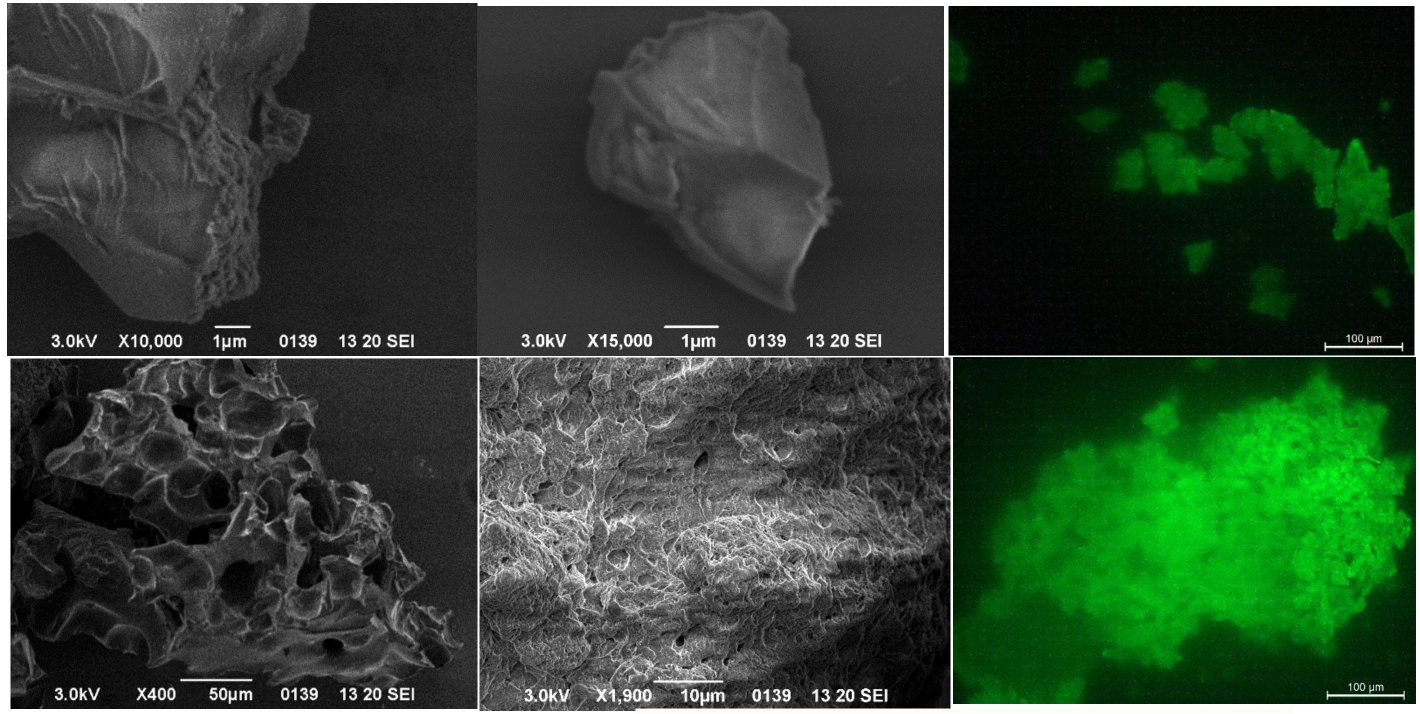
AEAPTMS:PNC mol ratio (6:1)



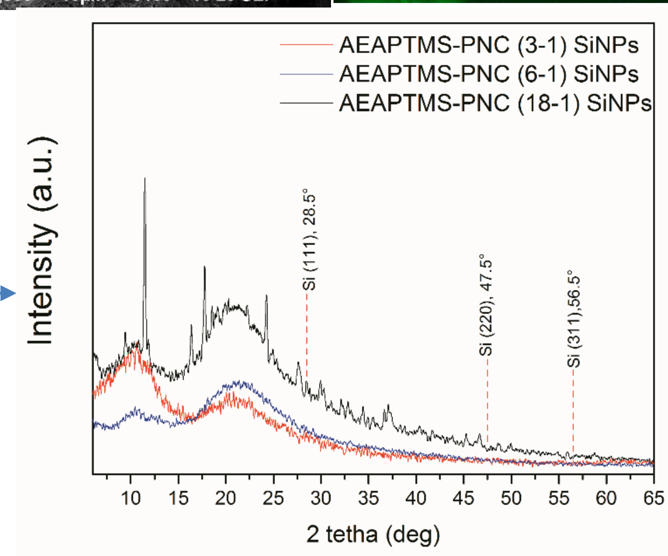
AEAPTMS-PNC assembled Silicon nanoparticles

AEAPTMS:PNC mol ratio (12:1)

AEAPTMS:PNC mol ratio (18:1)

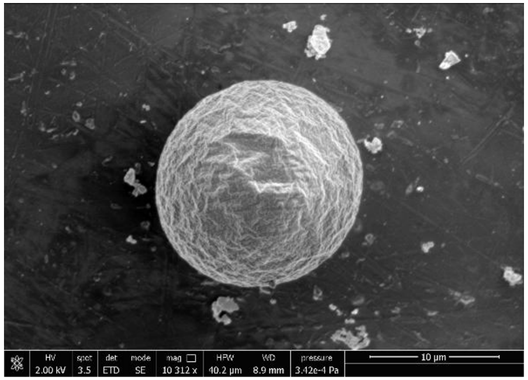


Crystallinity can be enhanced by modulation of silicon: cyclophosphazene mol ratio



Summary

APTMS:PNC

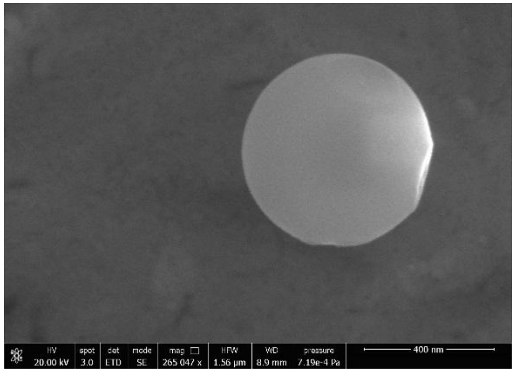


Wrinkled surface

Polydispersed with a wide PSD (up to 100 um)

Spherical morphologies
Different textural properties
Different crystalline properties

AEAPTMS:PNC



Smooth surface

Less polydispersed with broad PSD (around 1 um)

- **Template and surfactant free well define structures**
- **Fluorescent dye, gain medium and heavy metals no needed…**
- **Simple, fast and high yield approach…**

Tuning morphology, crystallinity and particle size

Very complex architectural structures

Acknowlegments

People

Prof. Maria Rosaria Tine´
Dr. Celia Duce
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Dr. Carlo Ferrari
Dr. Iginio Longo
INO-CNR area di Pisa

Prof. Giuseppe Barillaro
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Thank you for your attention!