Realities of fabricating nanomaterials: Past, Present and Future Prospects

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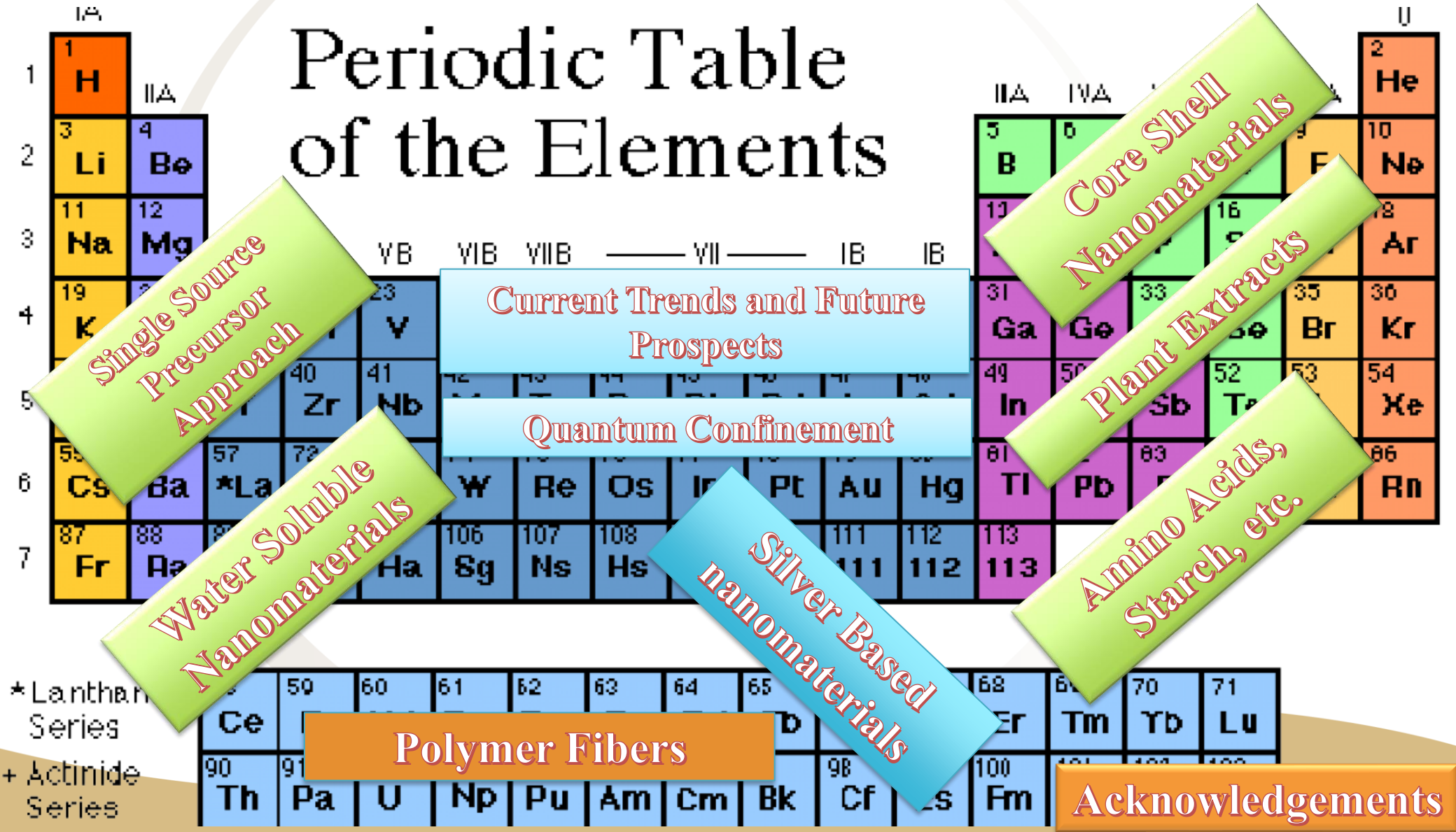
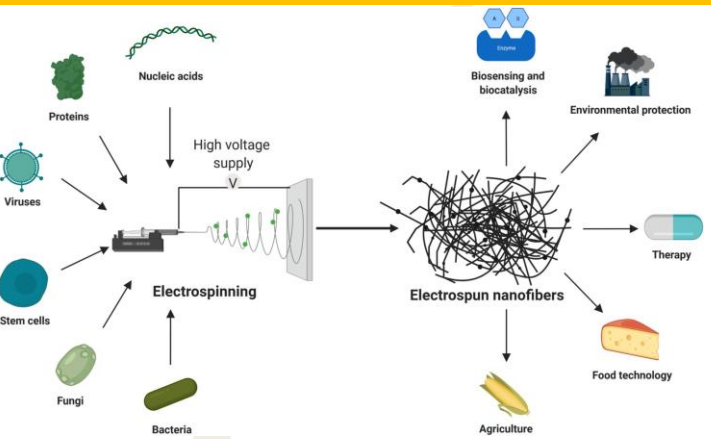
Define tomorrow.

UNISA college of science, engineering and technology

Outline of the Talk

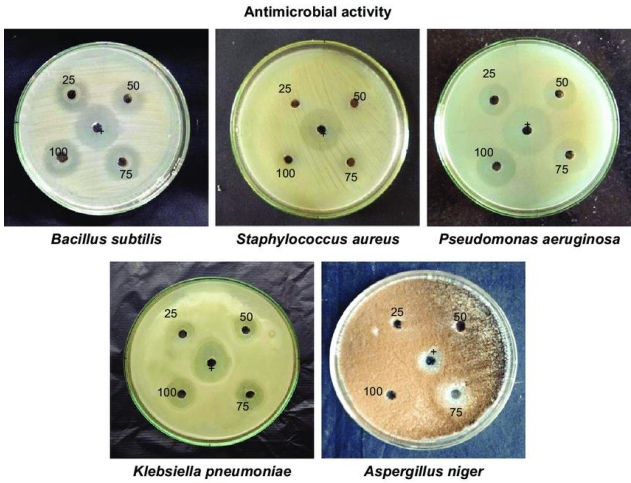


Current Trends

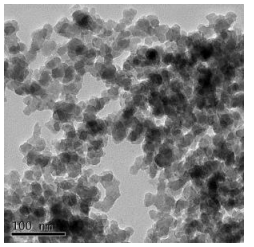


Nanofibers

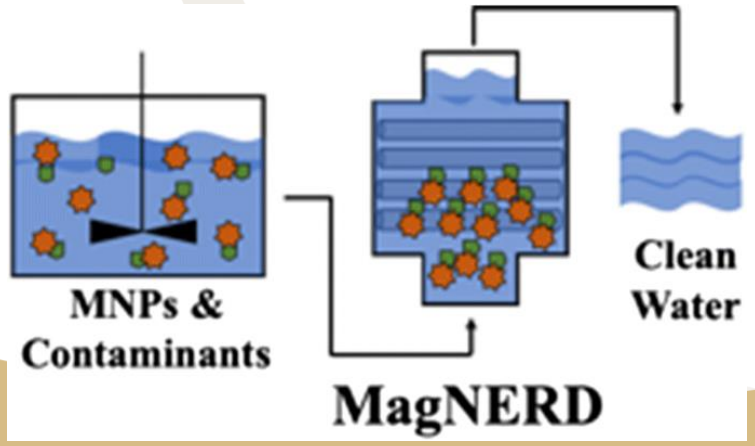
Silver NPs

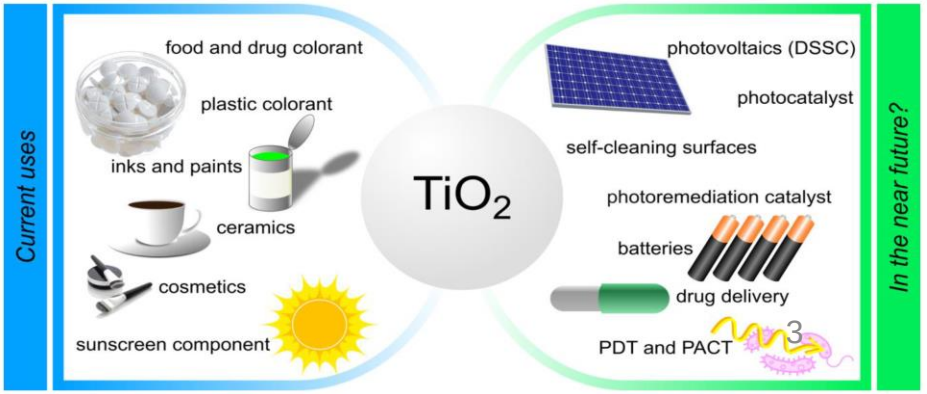


Titanium oxide NPs



Iron Oxide NPs

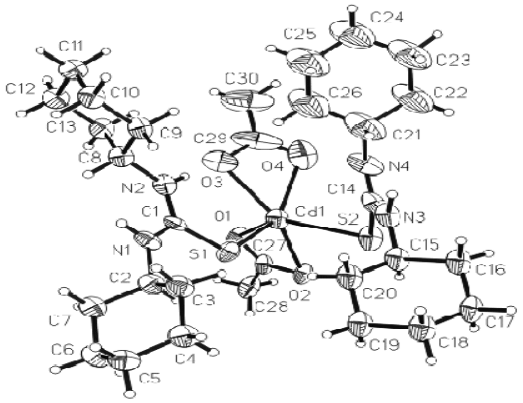




Single-source precursor route: Synthesis of complexes and nanoparticles

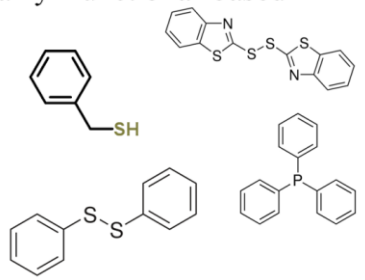
$Cd(CH_3COO)_2$
+
$SC(NHC_6H_{11})_2$

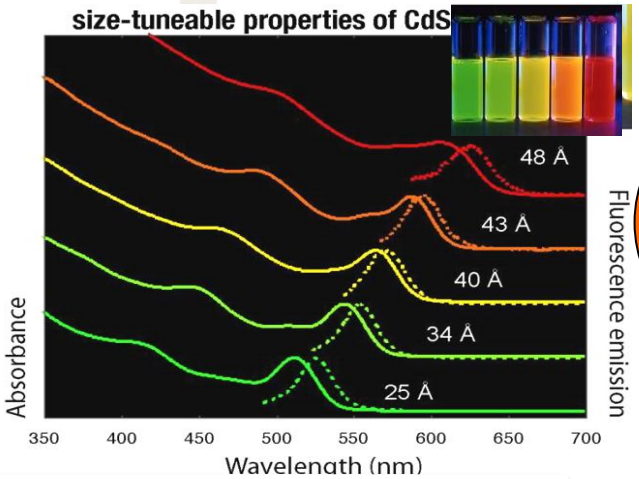
Reflux for 10 min-2 hours



Types of Ligands used in SSP

- Thiourea/Urea and alkyl functional based
- Dithiocarbamates
- Alkyl/arylthiolates
- Benzothiazoles
- Arylthiolates
- Alkoxides
- Arylphosphines

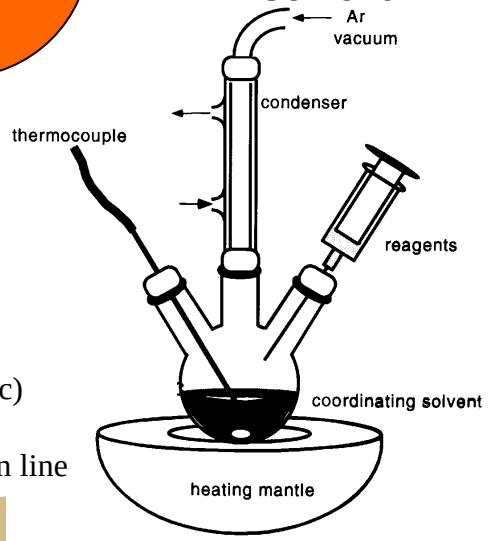




CdS

Molecular structure of $[Cd(CH_3COO)_2((CS(NHC_6H_{11})_2)_2]$

Thermolysis in a hot solvent

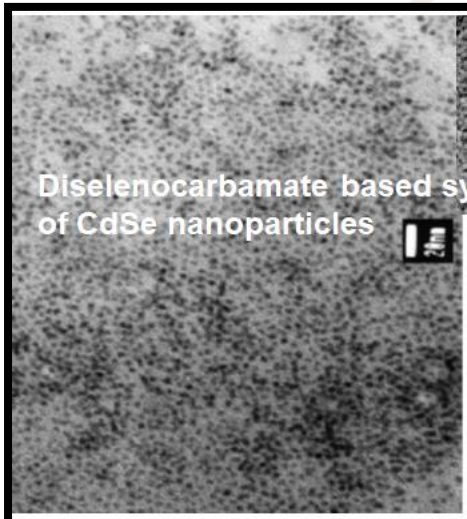


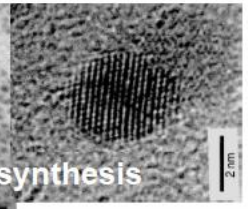
SSP approach proved simple, possible to minimize toxicity and produced very uniform controlled sizes and shapes of nanoparticles

RB Flasks
Condensers
Glass Syringes
Stirrers (magnetic)
Thermometer
Nitrogen or argon line
Heating mantles
Stirrers

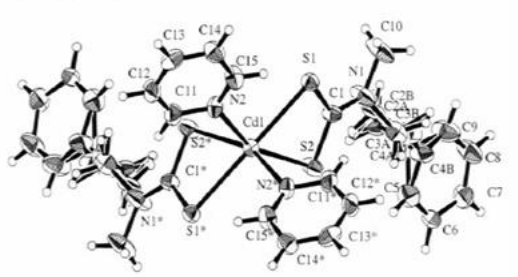
Cd = O, S, Se, Te - P
Pb = O, S, Se
Cu = O, S, Se
Co = O, S, Se - P
Mn = O, S, Se
Zn = O, S, Se
Ni = S, Se - P
GaAs, GaP

Single-source precursor route: Examples





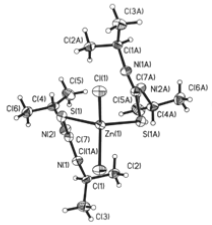
SAED pattern showing crystallinity



$Cd(Se_2CNRR')_2$ »»»»»⇒ CdSe.

O'Brien et al Chem Comm, 1998 1849, ibid 1999, 573

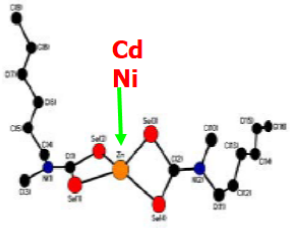
Dithio/seleno-carbamate based synthesis of MS/Se nanoparticles



Zn-S bonds

Under controlled thermolysis

ZnS



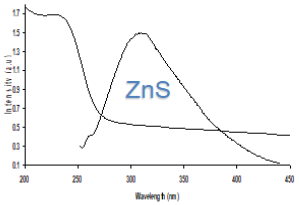
Zn-Se bonds

Under controlled thermolysis

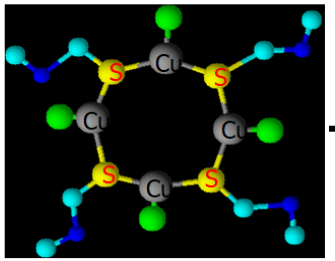
ZnSe

CdSe

NiSe



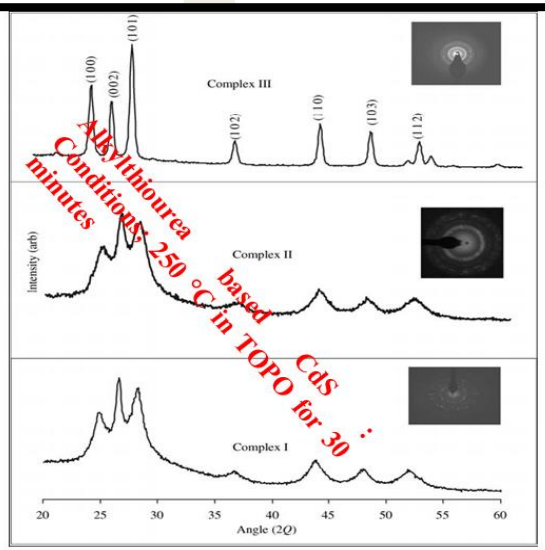
band edge - 266 nm
emission maximum - 312 nm



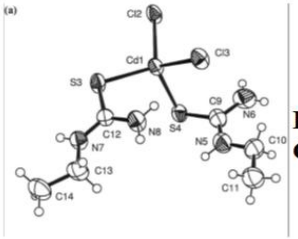
Cu-S bonds

Under controlled thermolysis

Cu_xS_Y



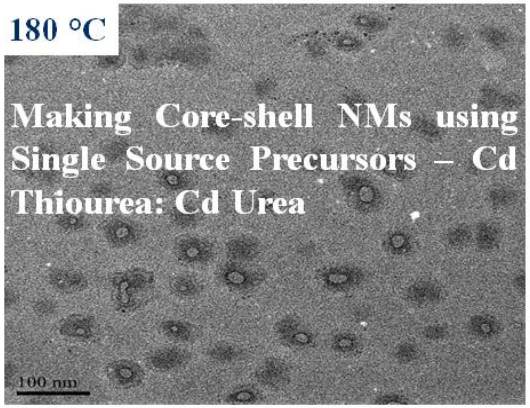
Thiuorea Cd complex

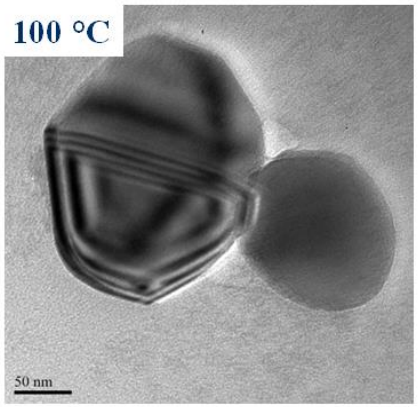


Ethylthiuorea Cd Complex

Methylthiuorea Cd complex

Journal of materials science, materials in electronics, 15 (2004), 313

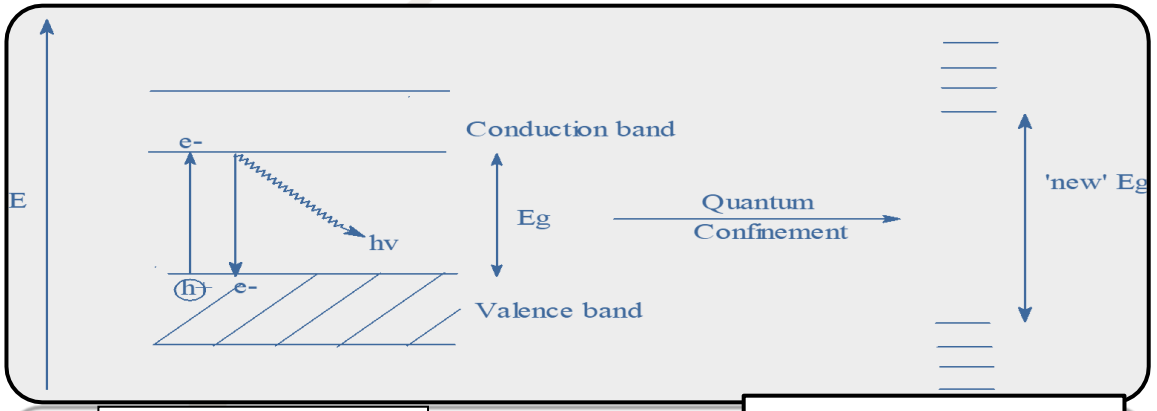




Hexadecylamine capped Nanoparticles (1:3) CdO-CdS

Particles with holes and Onion like structures

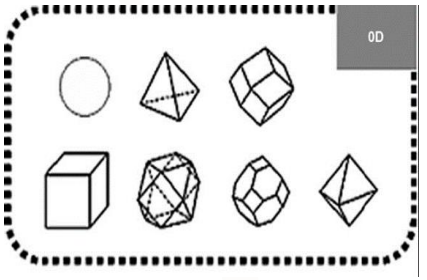
Quantum confinement



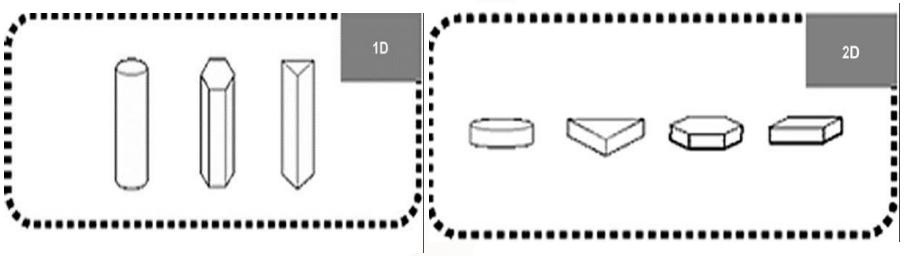
Bulk	Nanoparticles
CdS: 515 nm	< 500 nm
MnS: 400 nm	< 400 nm
PbS: 3351 nm	< 700 nm
CdSe: 712 nm	< 700 nm
CdTe: 827 nm	< 800 nm

Due to the spatial confinement of the charge carriers, the edge of the valance and conduction bands split into discrete, quantized, electronic levels. These electronic levels are similar to those in atoms and molecules.

SHAPES OF NANOPARTICLES



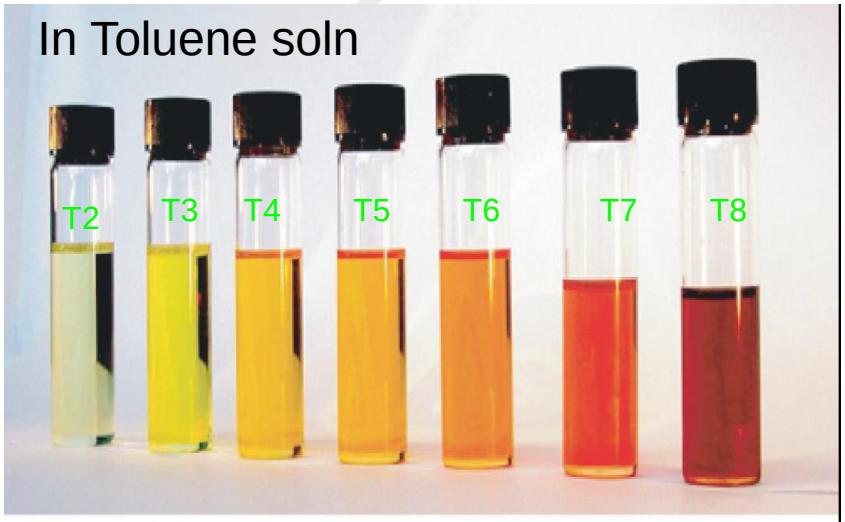
Spheres, rods, cubes, stars, wires, hexagons, tubes

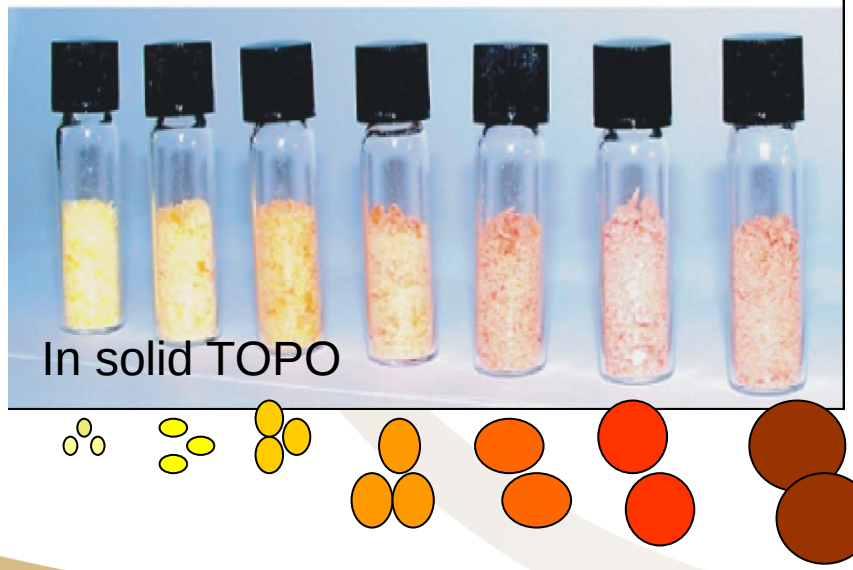


Basic motifs of inorganic nanocrystals: 0D spheres, cubes, and polyhedrons; 1D rods and wires; 2D discs, prisms and plates.

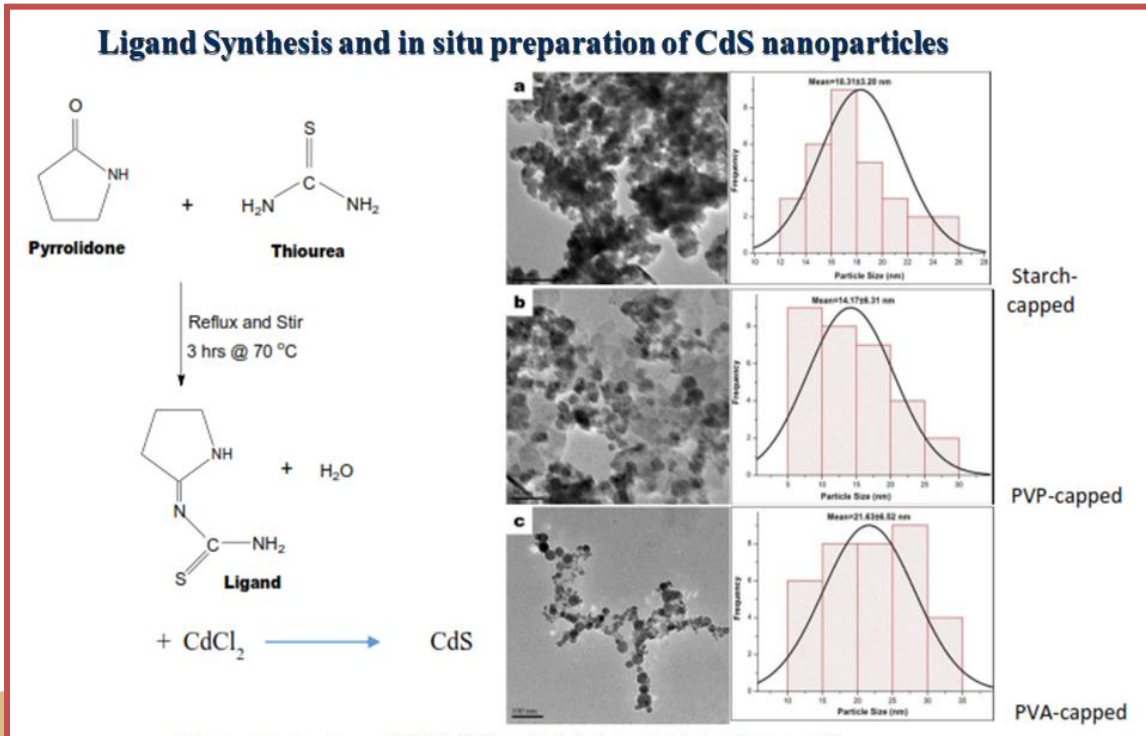
Synthesis Conditions in SSP and other approaches

TOPO = trioctylphosphine oxide





- **Types of Ligands/Variety of Complexes**
- **Time**
- **Temperature**
- **Solvent medium (Capping agents)**
- **Amounts of Solvent or Complexes**
- **Complex ratios as in core shell NM's**



Materials Letters, 2015, Xaba T, Moloto MJ & Moloto N

Coreshell Nanomaterials

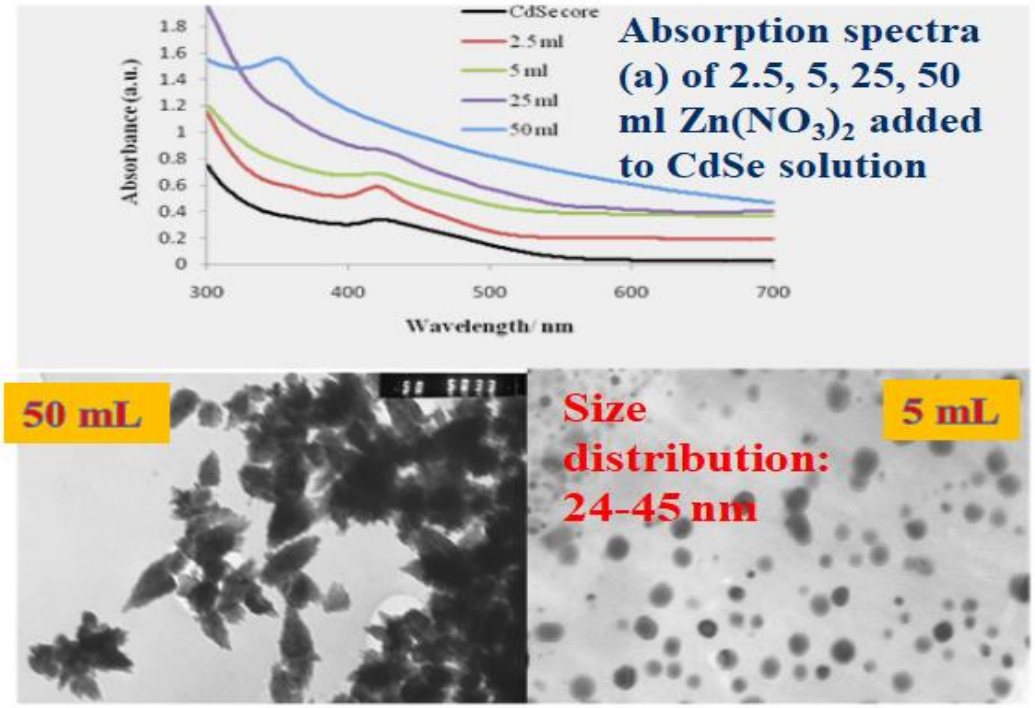
Synthesis of CdSe/ZnO and CdSe/PbS coreshell nanomaterials were prepared by adding a solution of PbS and ZnO into the CdSe solution by controlling pH and concentration of the reactants.

CdSe/ZnO Coreshell Nanomaterials

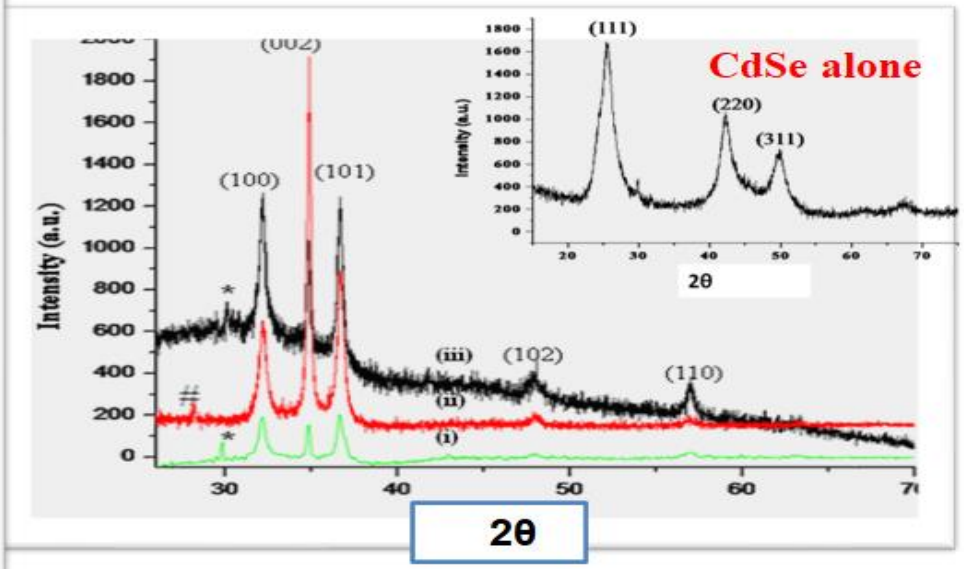
$NaBH_4 + Se + Cd^{2+} \rightarrow CdSe$

$Zn^{2+} + NaOH \rightarrow ZnO$

CdSe/ ZnO

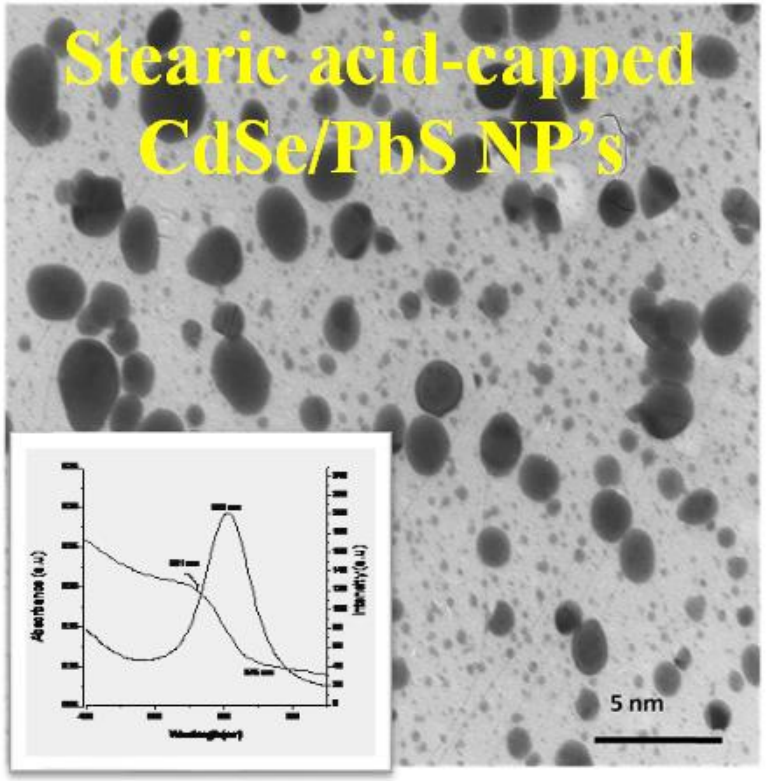


TEM images of CdSe/ZnO coreshell nanomat -erials prepared using 5 ml and 50 ml of 0.05 M $Zn(NO_3)_2$ and in 5 minutes at 40 °C. and pH 12.

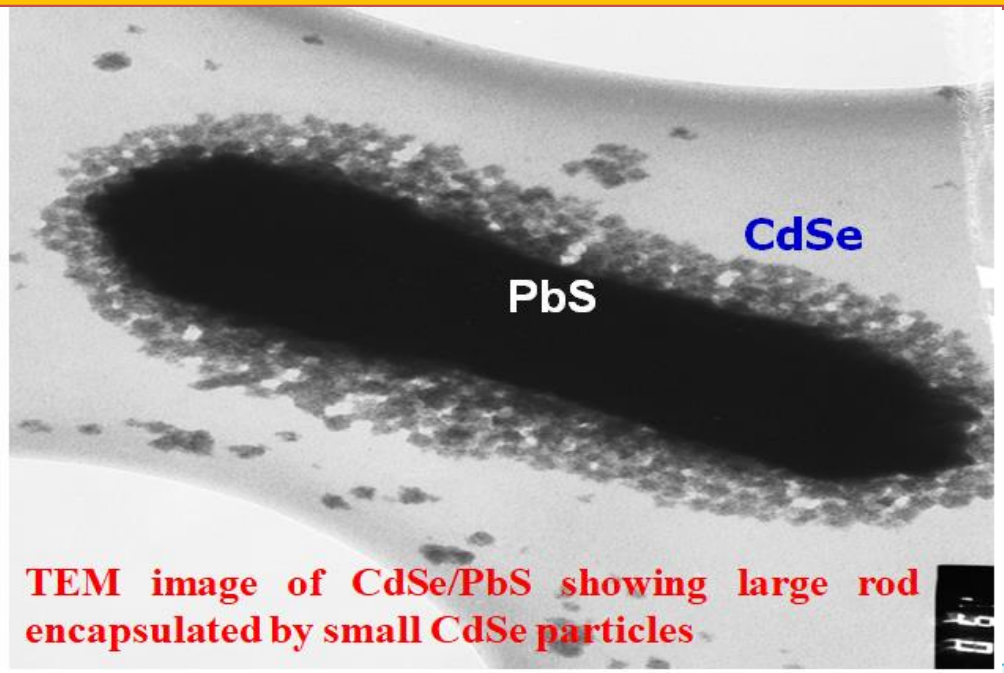


XRD patterns of CdSe/ZnO coreshell nanomaterials prepared using volumes – 2.5 mL(i), 5.0mL(ii), 50 mL(iii) of Zn^{2+} solution

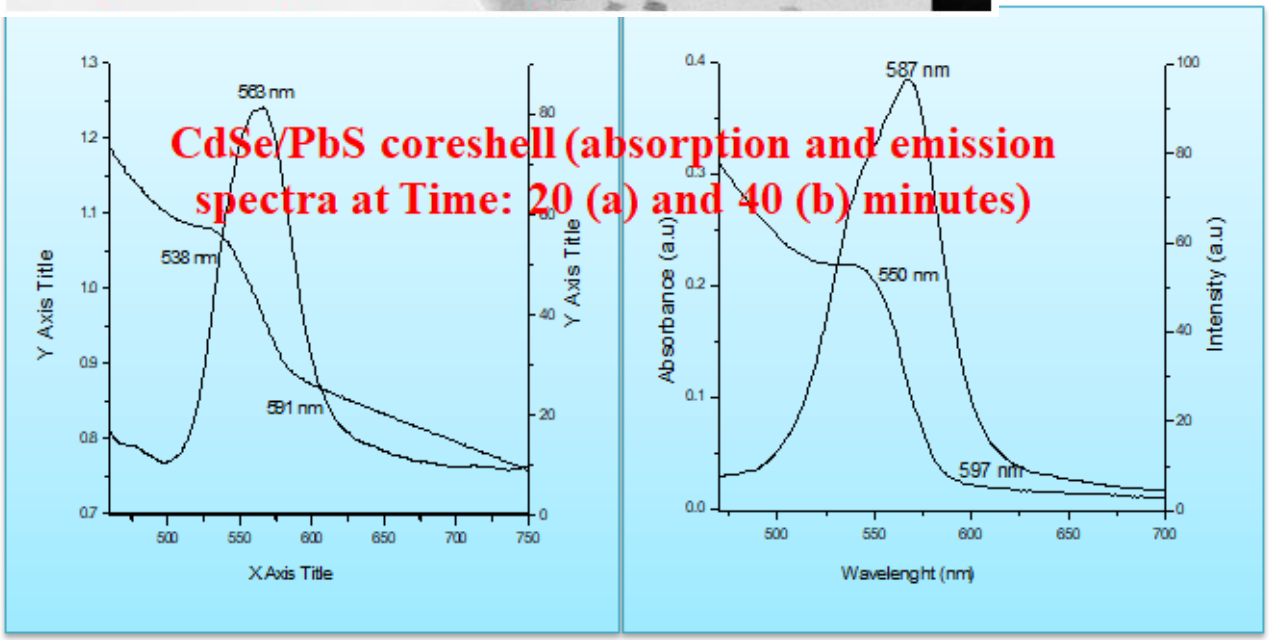
Examples of Core Shell NPs/Attempts



Absorption and emission spectra Resemblance of CdSe but red-shifted. TEM image: Spherical intensely dark centred nanoparticles.



TEM image of CdSe/PbS showing large rod encapsulated by small CdSe particles



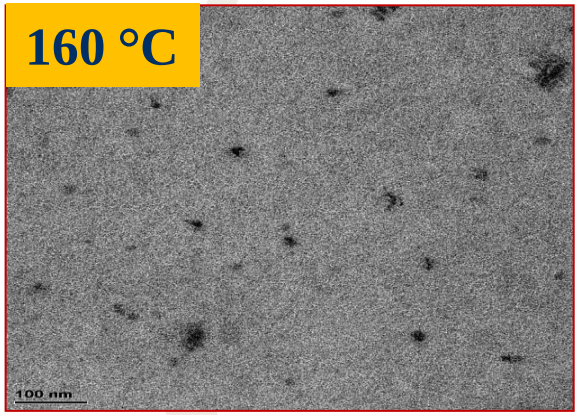
CdSe/PbS coreshell (absorption and emission spectra at Time: 20 (a) and 40 (b) minutes)

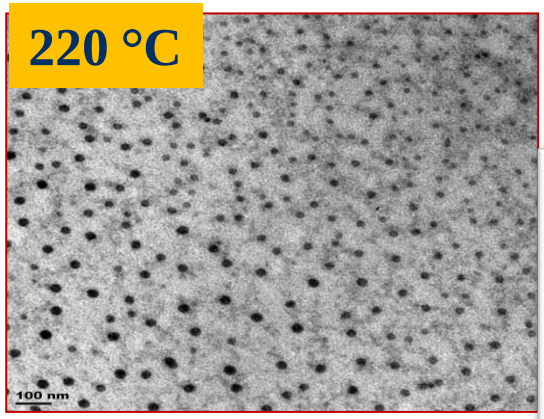
Single-Source Precursors: Shortcomings

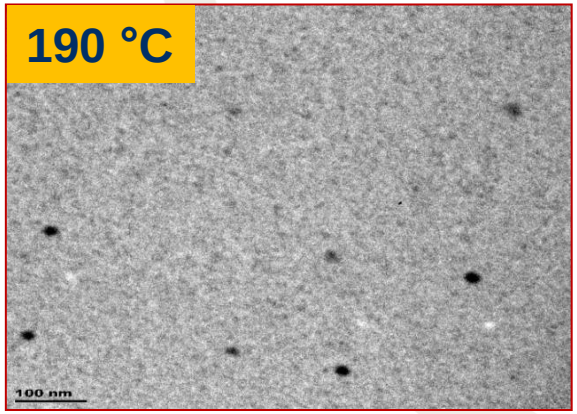
- Toxicity although possible to minimize, remains a problem
- Decomposition of organic moieties introduced additional step of purification.
- Operating at higher temperatures for better control of particle shapes and sizes.
- **Making nanoparticles water soluble for adaptation towards biomedical applications was a challenge**

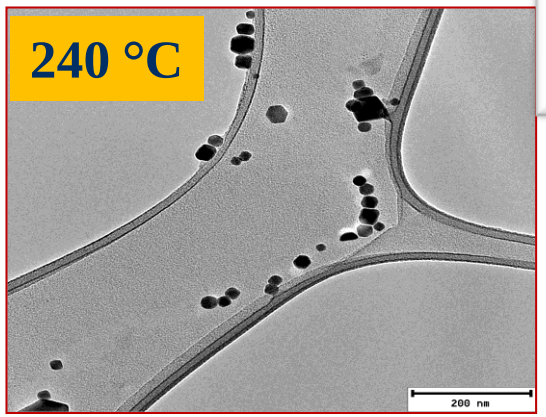
Oleyl amine Capped Cu_2Se NP's: Temp variation - higher

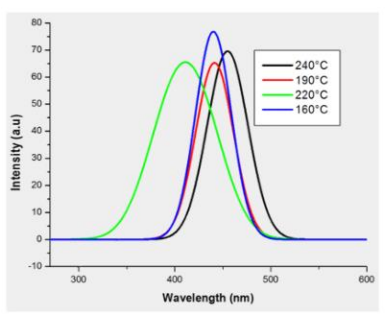
TEM images of CuSe NP's synthesized at different temperatures



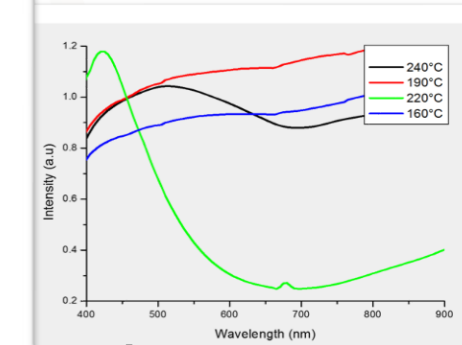








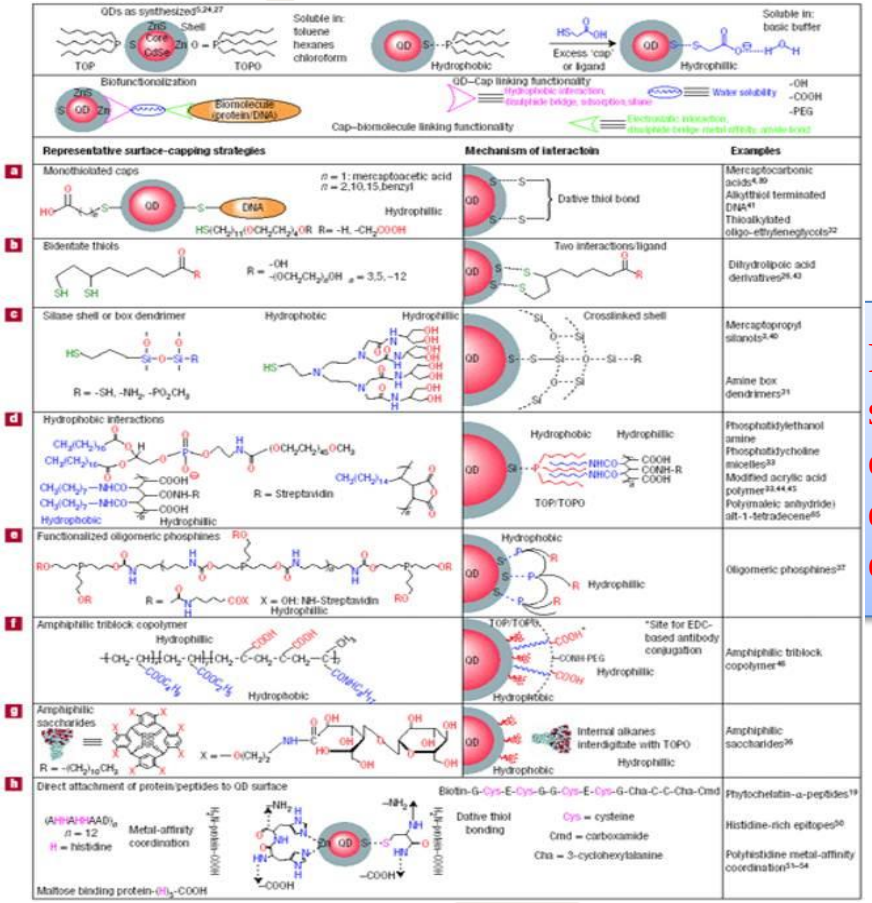
Emission spectra



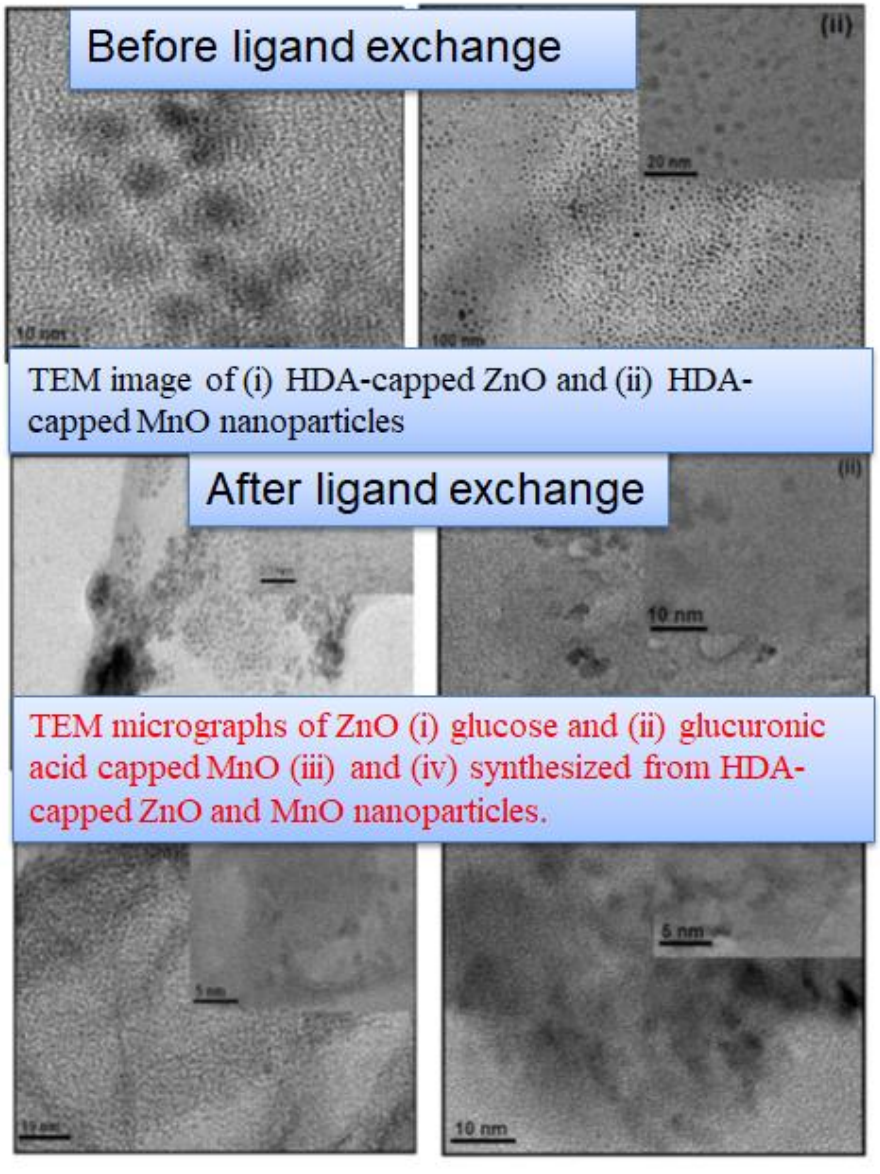
Absorption spectra

Ligand Exchange of Nanoparticles: Making the Water Soluble

Towards Biocompatible water soluble nanoparticles



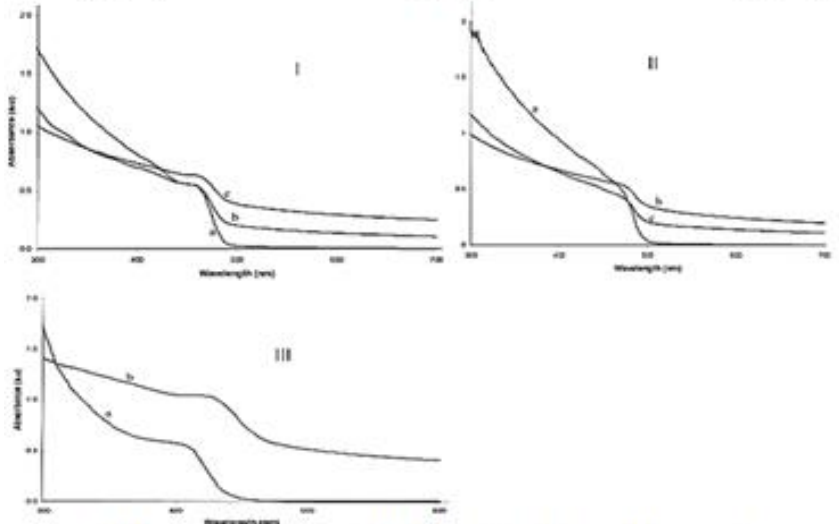
Particles losing shape and crystallinity – due to changes on the surface



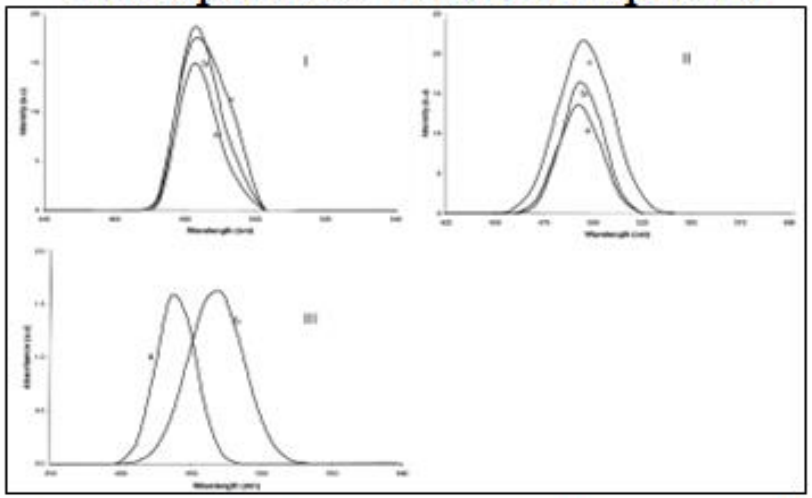
Nature Materials (Medintz IL, Uyeda HT, Goldman ER, Mattoussi H. Quantum dot bioconjugates for imaging, labelling and sensing. Nat Mater. 2005; 4: 435-46., http://www.nature.com), copyright 2005.

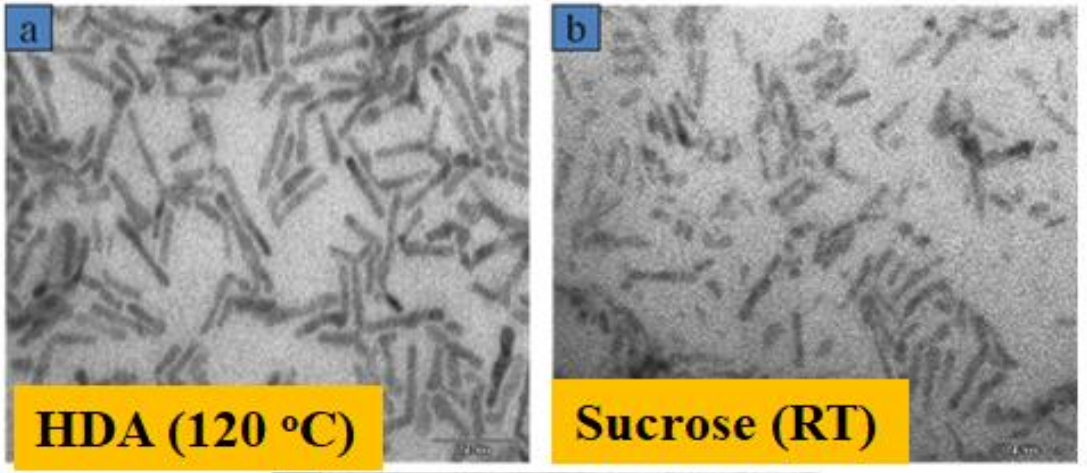
Scenarios/Approaches

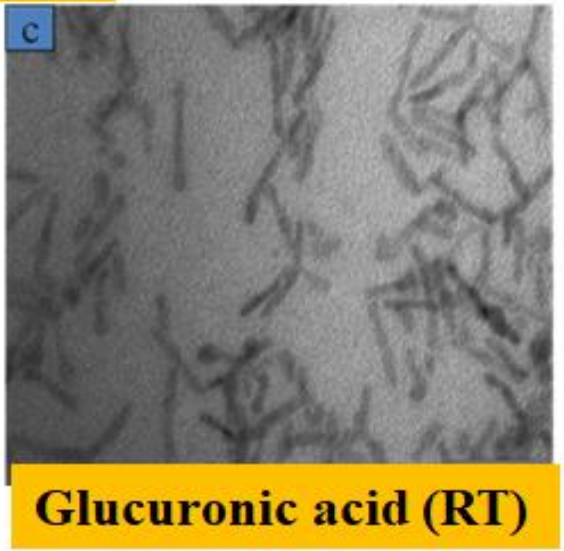
CdS NPs capped by (I) (a) HDA (120 °C), (b) sucrose (RT), (c) glucuronic acid(RT), (II) (a) HDA (180 °C), (b) sucrose and (c) glucuronic acid, (III) (a) TOPO (180 °C) and (b) glucuronic acid (80 °C)



Absorption & Emission Spectra



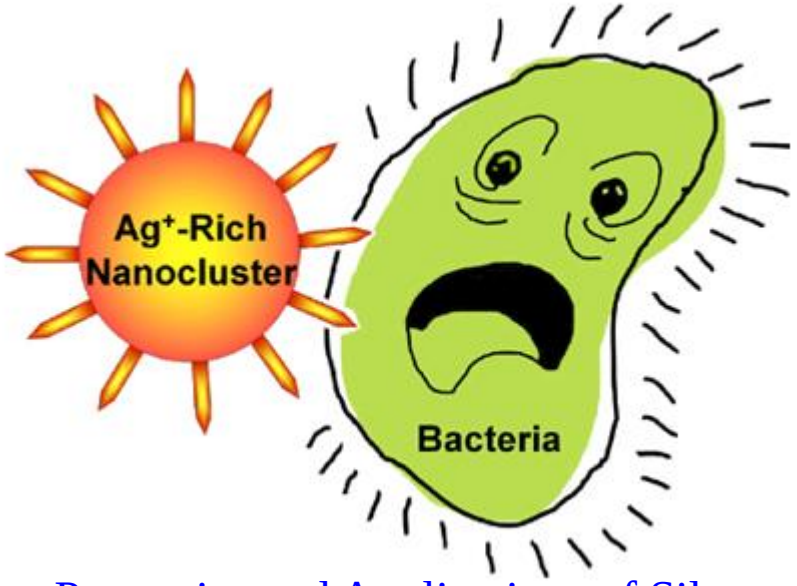




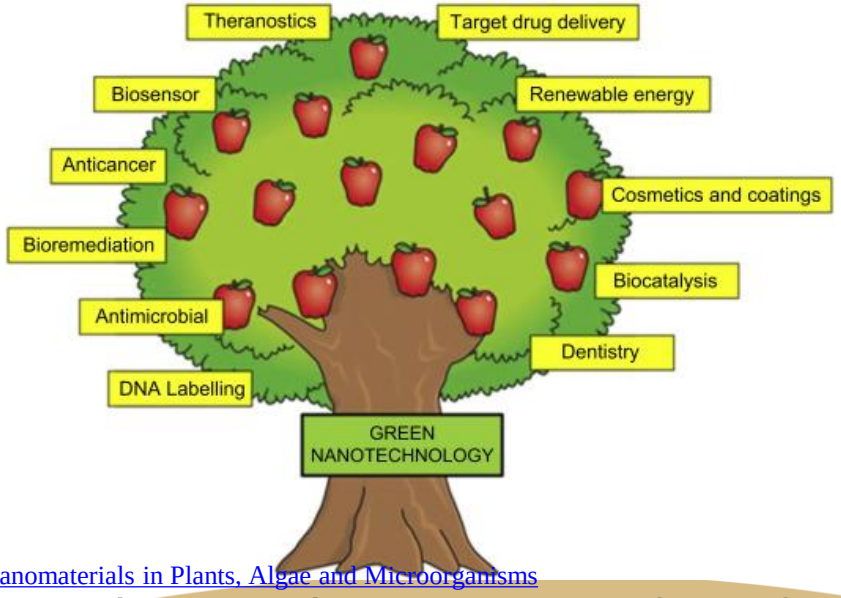
TEM images

Digest Journal of Nanomaterials and Biostructures, Vol. 12, No. 1, 2017, p. 195 - 204 : PM Shumbula & MJ Moloto

Silver Based Nanomaterials & Plant Extracts

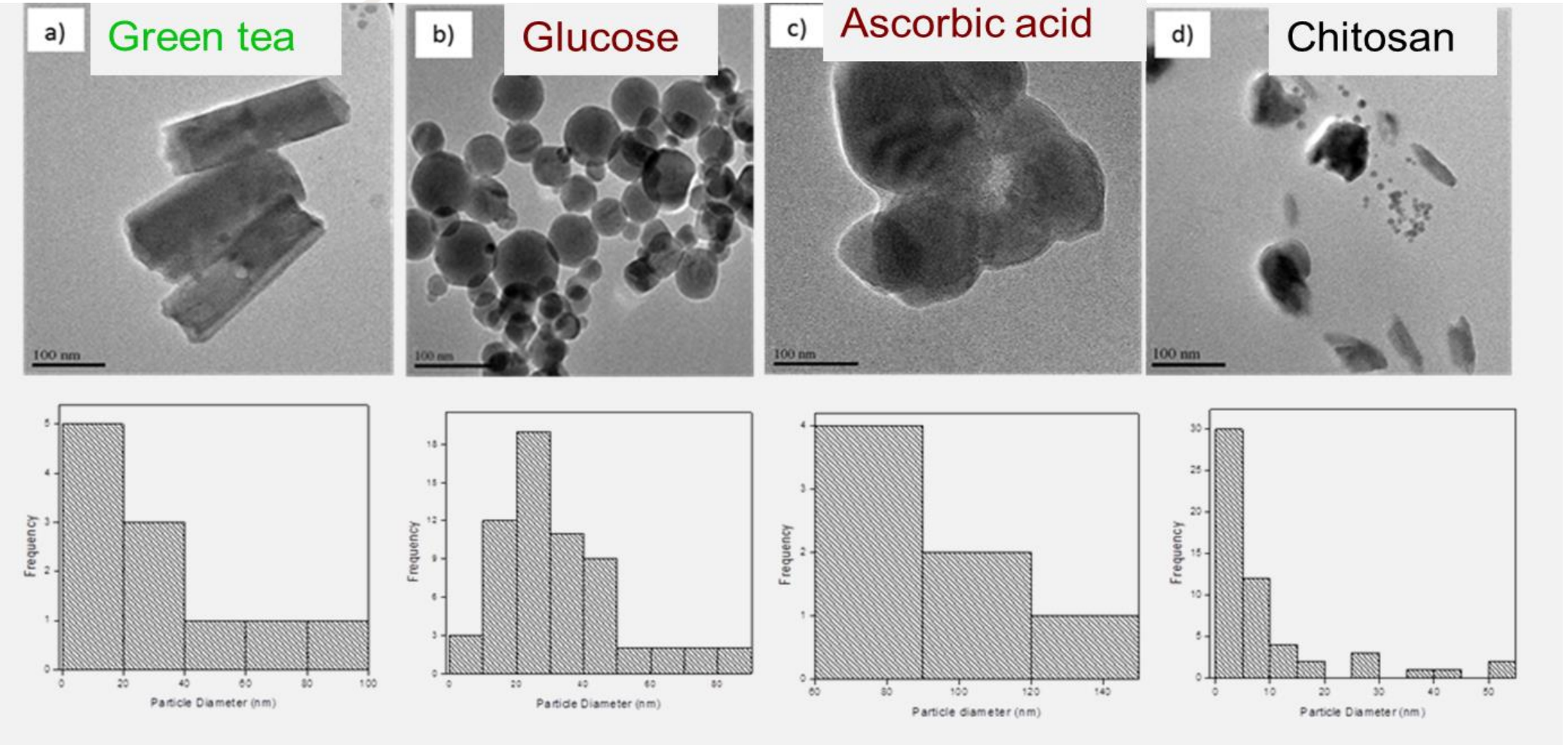


Properties and Applications of Silver Nanoparticles - CD Bioparticles (cd-bioparticles.com)



Nanomaterials in Plants, Algae and Microorganisms
Concepts and Controversies:volume 2; 2019, Pages 169-196; Chapter 9 - Therapeutic Potential of Plant-Based Metal Nanoparticles: Present Status and Future Perspectives; Author links open overlay panelAbhishek KumarDwivedy[1]NehaUpadhyay[1]SimranAsawa[2]ManojKumar[1]BhanuPrakash[1]Nawal KishoreDubey[1]

Ag_2Se NP's: Various Green Capping Molecules

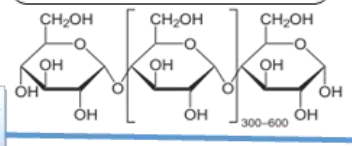


The TEM micrographs and size histograms of Ag_2Se nanoparticles capped with 1.0 % (w/v) solutions.

Green Processing and Synthesis; 2017; 6: 183–188, PN Sibiya & MJ Moloto

Starch as a Capping Agents: Ag_2O, Ag_2Se & Ag_2S & Ag_2Se Extraction time and Concentration variations

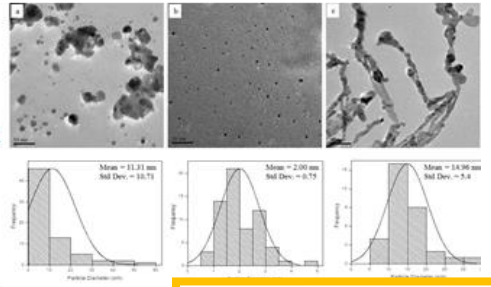
Starch-capped Ag_2O Nanoparticles



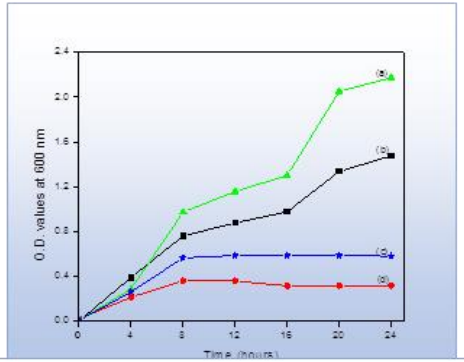
$AgNO_3$ (20 mL, 0.1 M) + NaOH (20 mL, 0.1 M)

Capping molecule (0.5-2 % (w/v))

Ag_2O Nanoparticles



Journal of Materials Science, Materials in Medicine, 2017, PN Sibiya, MJ Moloto



Growth curves of a) Staphilococcus aureus alone, b) Escherichia coli alone, c) Staphilococcus aureus with Ag_2O nanoparticles, d) Escherichia coli wit Ag_2O nanoparticles.

Ag_2Se Extraction time and Concentration variations

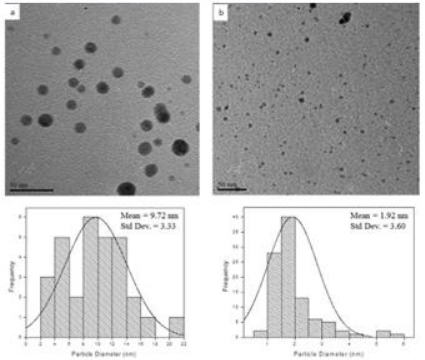
Sample	A	B	C	D	E	F	G
Capping agent Conc (%)	0.05	0.05	0.05	0.05	0.05	0.025	0.1
Extraction Time (hrs)	0	5	10	15	20	20	20

$$4NaBH_4 + 2Se + 7H_2O \longrightarrow 2NaHSe + Na_2B_4O_7 + 14H_2 \quad (1)$$

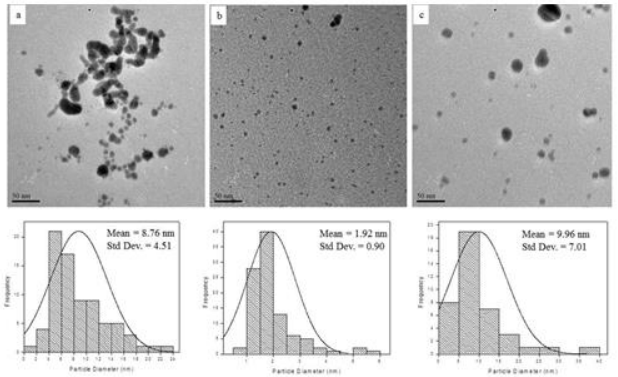
$$AgNO_3 + \text{Starch} \longrightarrow \text{Ag-starch complex} \quad (2)$$

$$\text{Ag-starch complex} + HSe^- + OH^- \longrightarrow \text{starch-}Ag_2Se + H_2O \quad (3)$$

$$HSe^- + OH^- \longrightarrow Se^{2-} + H_2O \quad (4)$$



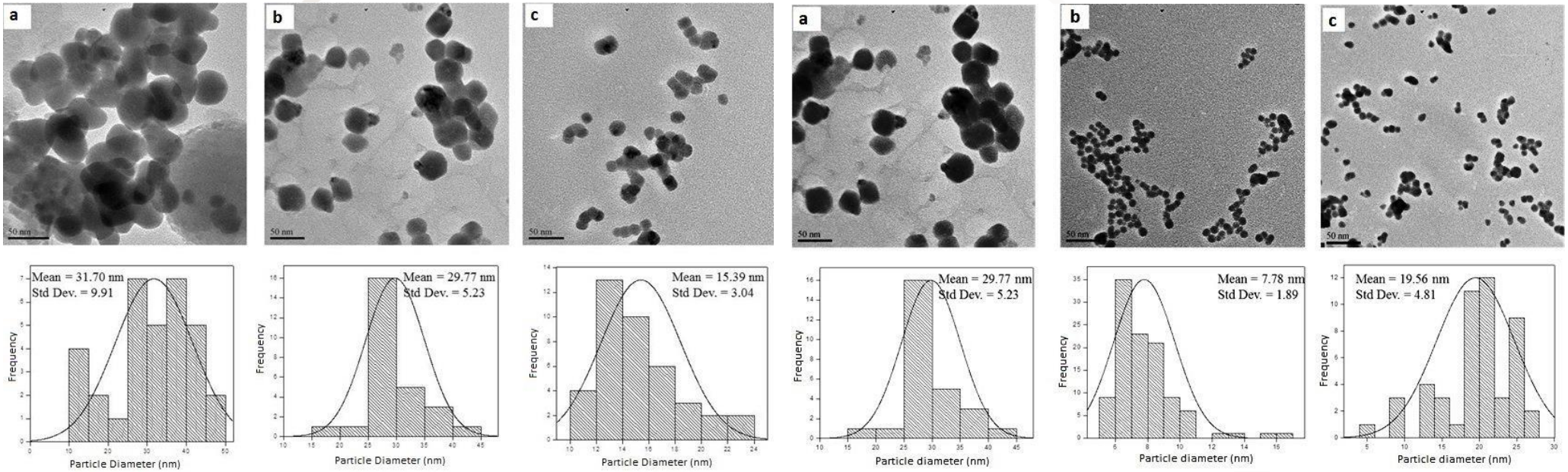
TEM images and histograms for starch capped Ag_2Se nanoparticles prepared at 15 hours (a) and 20 hours (b).



TEM images of starch capped Ag_2Se nanoparticles with 0.025 w/v (a), 0.05 w/v (b) and 0.1 w/v (c) starch.

Asian Journal of Chemistry; 2016, 28(6), pp. 1315-1320: PN Sibiya & MJ Moloto

Ag_2S NP's: Starch : silver nitrate ratio – Using Thiourea as sulphide source



TEM image and size histograms for starch capped Ag_2S (1 : 1) nanoparticles with (a) 0.5% (w/v), (b) 1.0% (w/v) and (c) 2.0% (w/v) starch

TEM images and size histograms for starch capped Ag_2S nanoparticles with 1.0% (w/v) starch (a) 1 : 1, (b) 1 : 2 and (c) 2 : 1

The antibacterial activity of Ag_2S nanoparticles against E coli and S aureus:

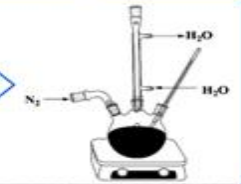
- **The lower precursor ratio had the lowest MIC value- less than 0.023 mg/ml,**
- **- While the higher precursor ratios had MIC value of 0.046 mg/ml.**
- **- The growth curve studies of bacteria treated with Ag_2S NPs showed an increase in growth and then a decrease as the exposure time was increased.**

Int. J. Nanotechnol., Vol. 14, Nos. 1/2/3/4/5/6, 2017 385: PN Sibiya & MJ Moloto

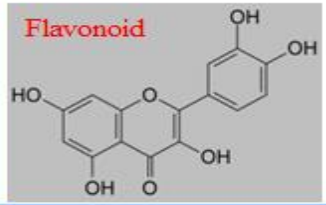
Plant Extracts: Silver NP's using Combretum Molle: ZnS on Eucomis autumnalis

Silver NP's using Combretum Molle: Plant extracts and Antimicrobial activity

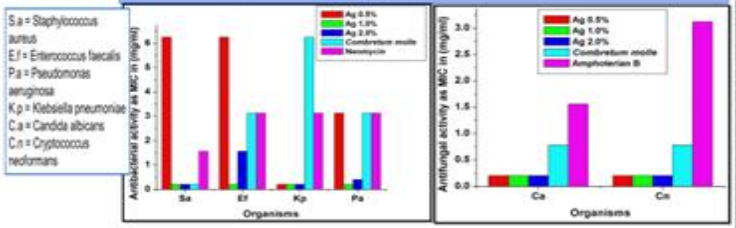
One step colloidal synthesis

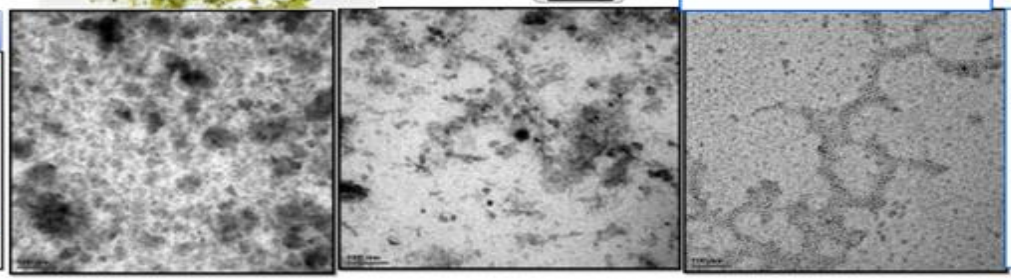


Reaction parameters
Temperature: 25 °C
Time : 2hours
$AgNO_3$: 0.1M
Extract : 0.5, 1.0 & 2.0%



Antimicrobial activity

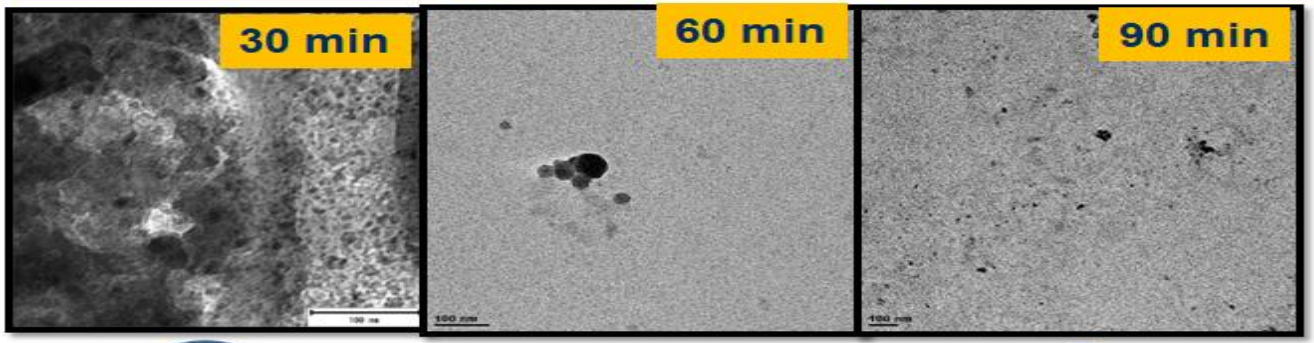


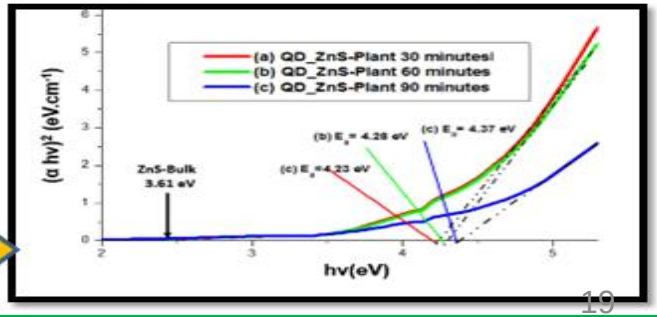


- Spherical particles with average size that ranges from 5-9 nm were obtained.
- Low degree of agglomeration was observed with an increase in capping agent concentration
- Decrease in particle size with an increase in capping agent concentration is attributed to increase in hydroxyl functional groups.

Silver nanoparticles showed good antibacterial and antifungal activity compared to aqueous extract of *Combretum molle* leaves, *neomycin* and *amphoterian B*

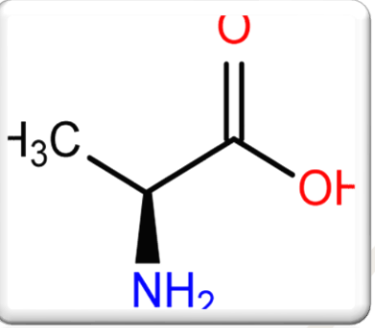
ZnS nanoparticles capped with medicinal plant extracts from Eucomis autumnalis - Time variation

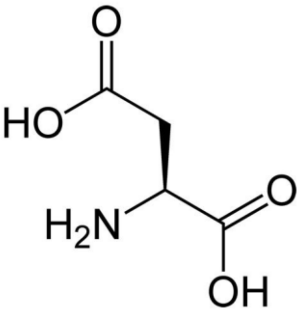


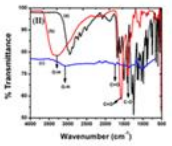


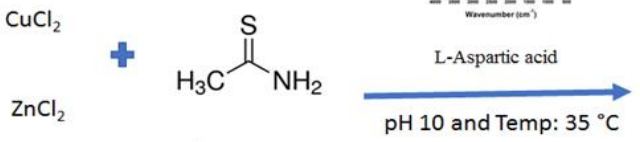
Energy increase as particle size becomes smaller

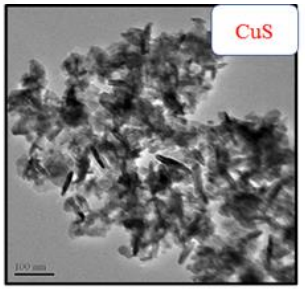
Amino Acids: CuSe, CuS & ZnS NP's: Cysteine, Alanine and Aspartic acid



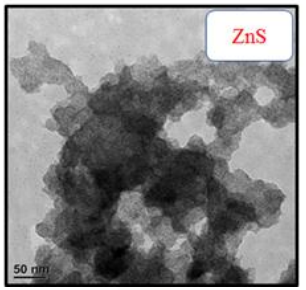




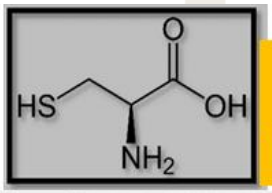




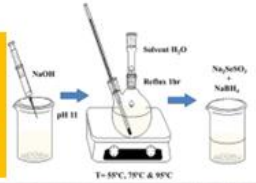
Bacterial strains	Asp-CuS
S. aureus	0.1
E. faecalis	0.78
K.pnuemoniae	0.39
P.aeruginosa	1.56
C.albicans	0.78
C. neoformans	0.391

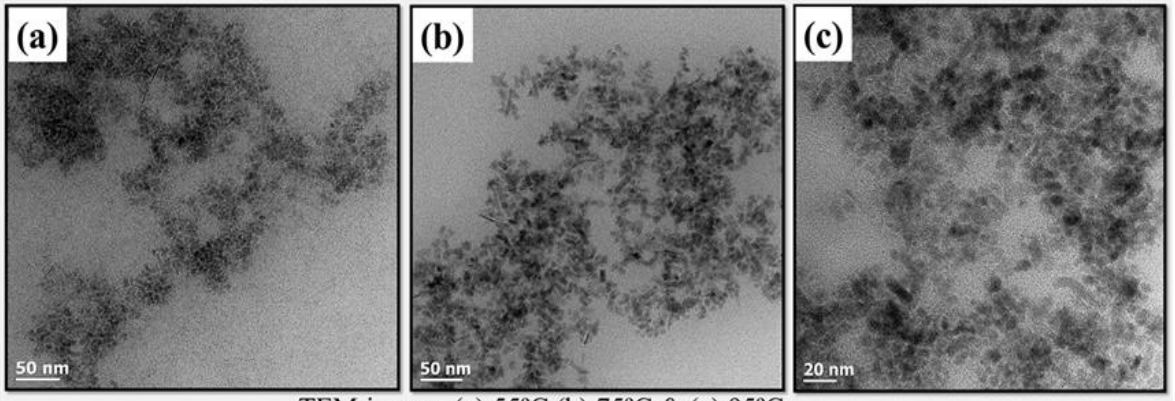


Bacterial strains	Asp-ZnS
S. aureus	6.25
E. faecalis	25
K.pnuemoniae	25
P.aeruginosa	0.78
C.albicans	25
C. neoformans	6.25



L-Cysteine Capped Cu_2Se NP's: Temp variation - lower



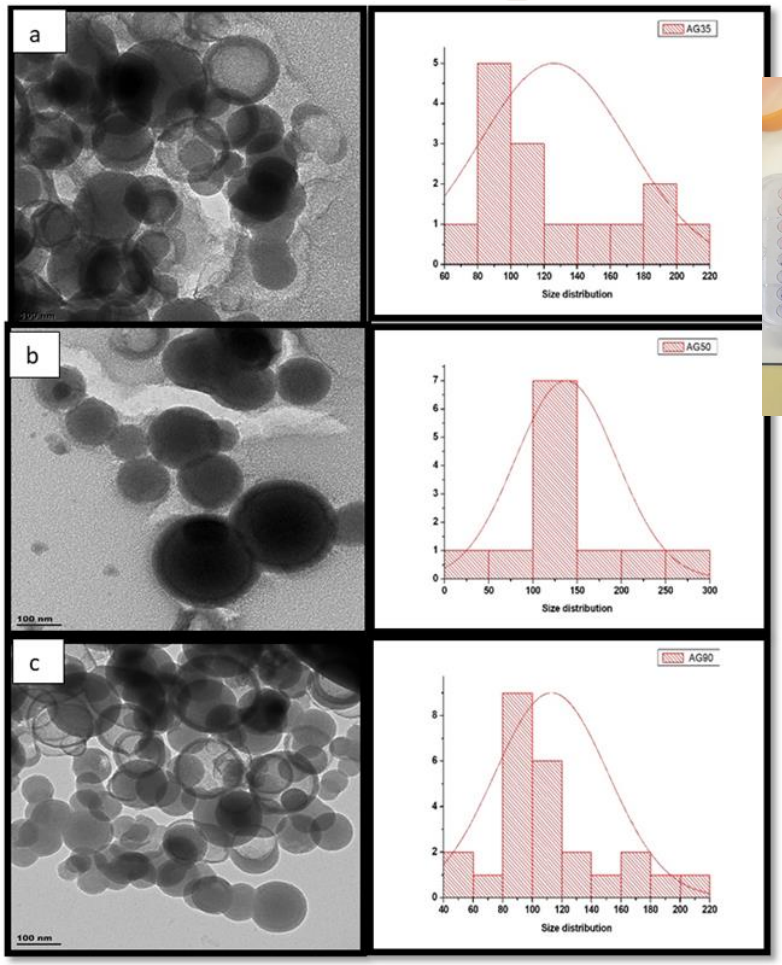


TEM images (a) 55°C (b) 75°C & (c) 95°C

- Strains of bacteria and fungi were tested against both ZnS and CuS nanoparticles with and without capping on the surface.
- CuS shows good antibacterial and antifungal activity with uncapped showing the least MIC, 0.05 mg/ml for Staphylococcus aureus.

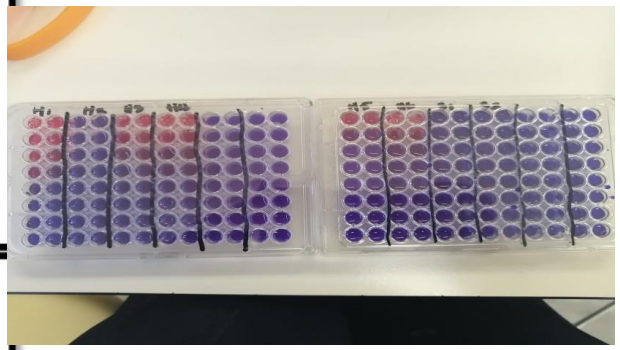
Journal of Nanobiotechnology; 2017, **TP Mofokeng**, MJ Moloto, PM Shumbula, P Nyamukamba, PK Mubiayi, S Takaidza & L Marais,

Peptide Bond Formation



TEM images of AG-capped TiS_2 nanoparticles synthesized at different temperature a) 35, b) 50 and c) 90 °C.

96 Well plates for various bacterial species



Before incubation

After 24 hrs of incubation

Bacterial growth rate for the selected species and nanoparticles

Material	Bacterium	Time it took for growth
1. L-glutamine capped TiS_2 nanoparticles	S-aureus	2 sec
	E-coli	57 sec
2. L-cysteine capped TiS_2 nanoparticles	S-aureus	Instantly
	E-coli	9 sec
3. CG- capped TiS_2 nanoparticles Temp: 90 °C & pH: 8	S-aureus	Instantly
	E-coli	3 sec
4. AG- capped TiS_2 nanoparticles Temp: 90 °C & pH: 6	S-aureus	Instantly
	E-coli	Instantly

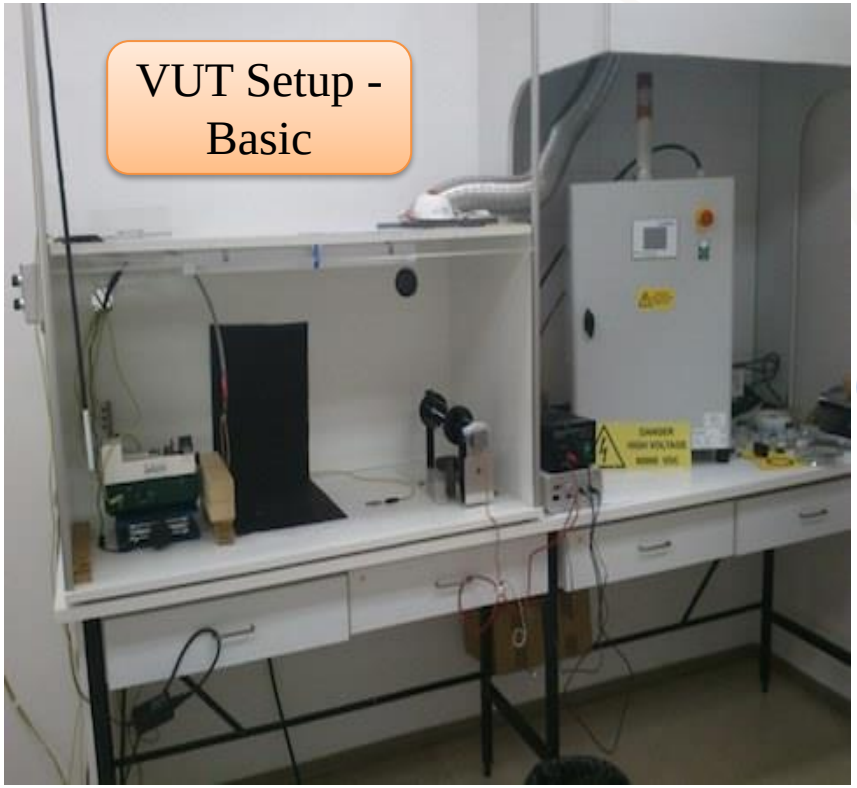
Polymer fibres - Electrospinning technique

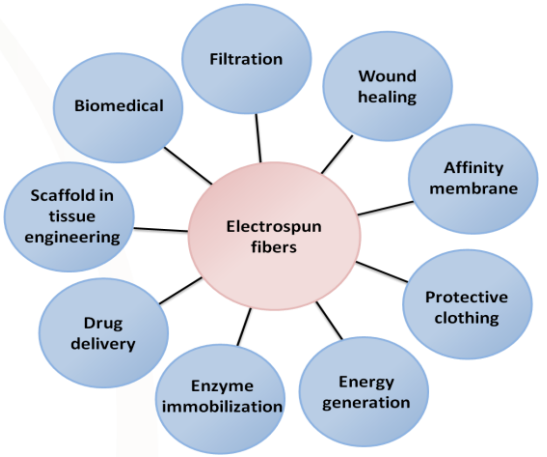
Electrospinning parameters

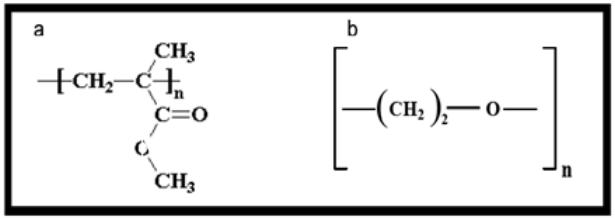
Polymeric solution + High Voltage = Polymer fibers (µm-nm)

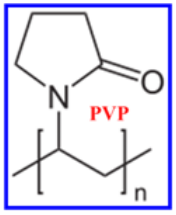
Fiber diameter can be tuned by modifying different conditions

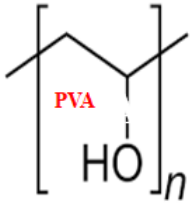
- Fiber diameter
- ES Conditions
  - Electric Field
  - Flow Rate
  - Tip-Collector Distance
- Solution properties
  - Viscosity
  - Conductivity
  - Surface Tension
- Ambient parameters
  - Temperature
  - Humidity
  - Air velocity



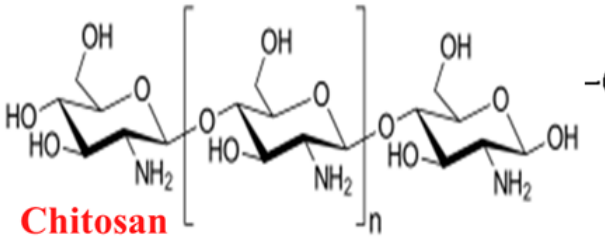


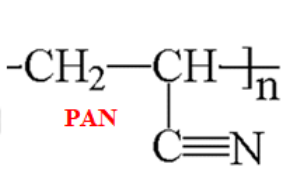


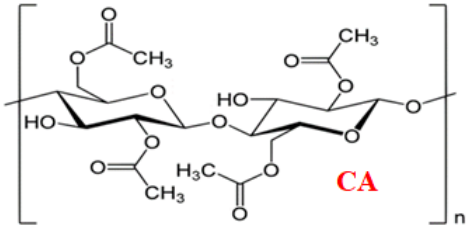




Polymers used for electrospinning

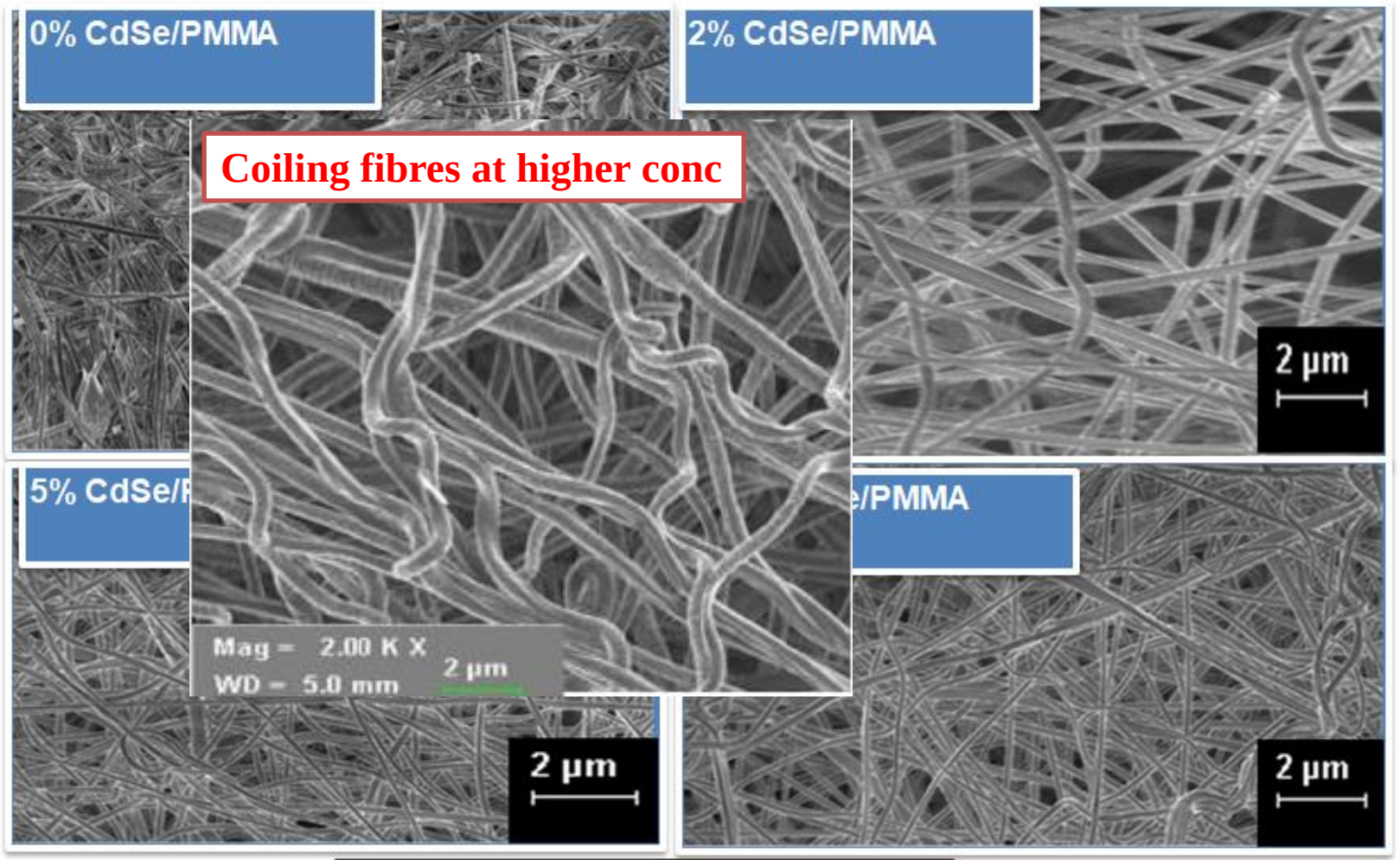






CdSe/PMMA/PEO polymer fibers

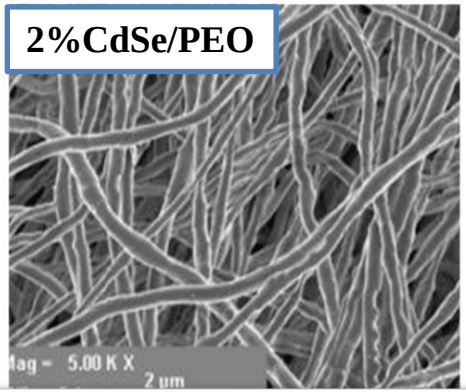
SEM Images of various CdSe percentages in polymer, PMMA

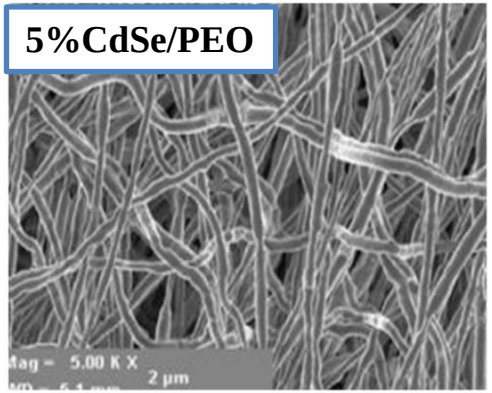


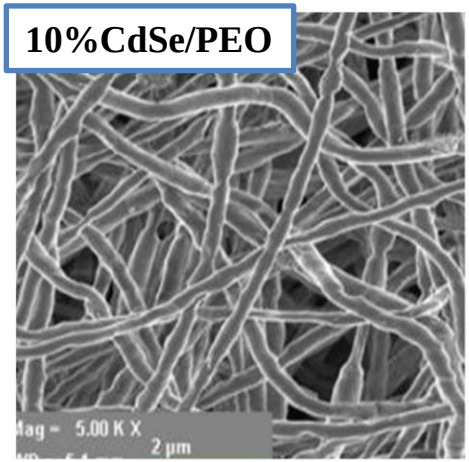
Diameters: 530 to 660 nm

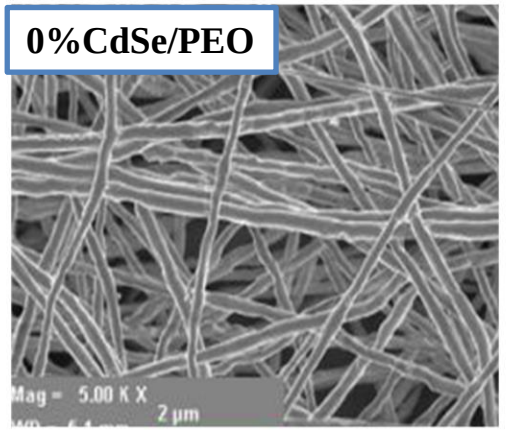
Observable features include coiling of fibres as the concentration of CdSe nanomaterials is increased especially at 10%CdSe (SEM image)

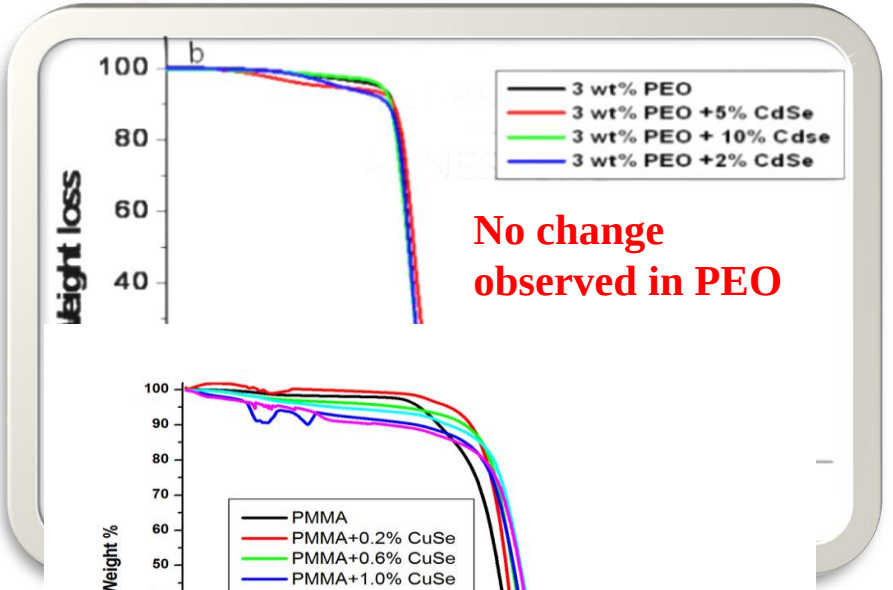
SEM Images of various CdSe percentages in polymer, PEO

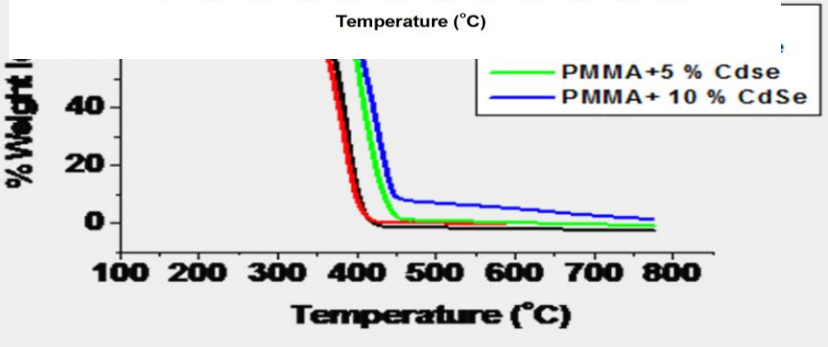






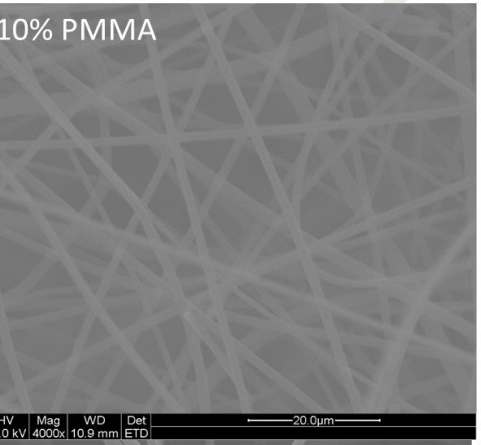


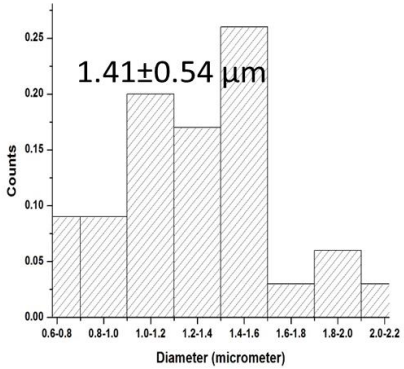


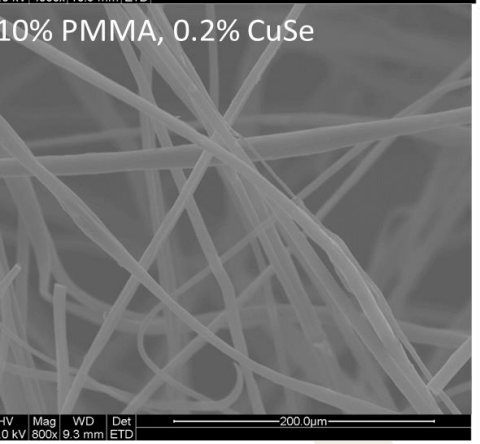


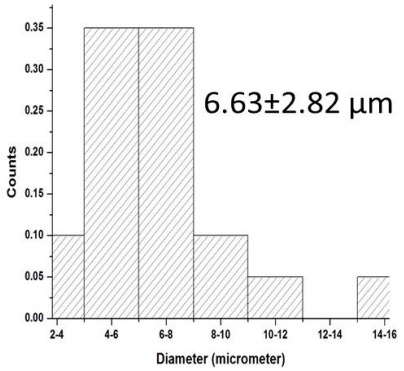
Diameters: 490 to 560 nm

CuSe/PMMA fibres

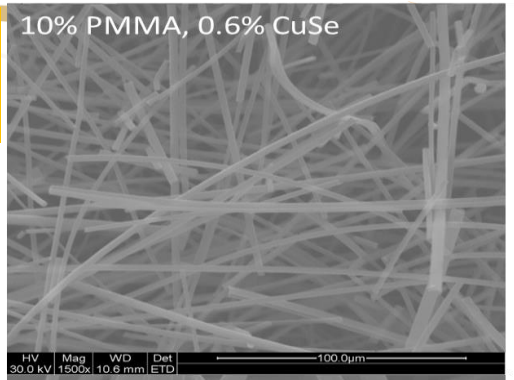


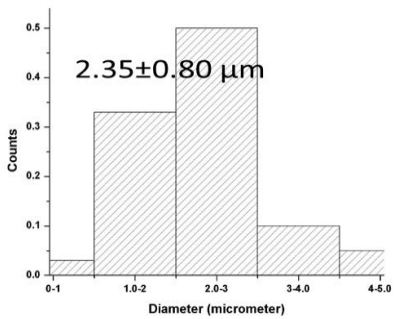


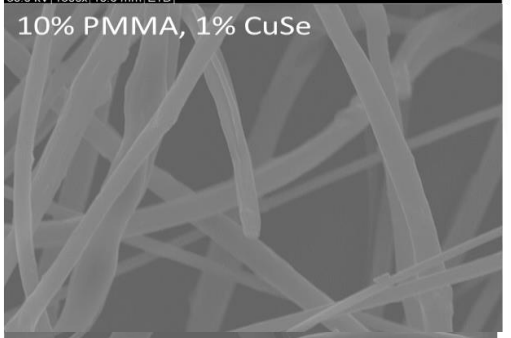


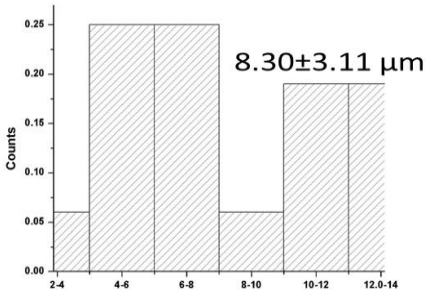


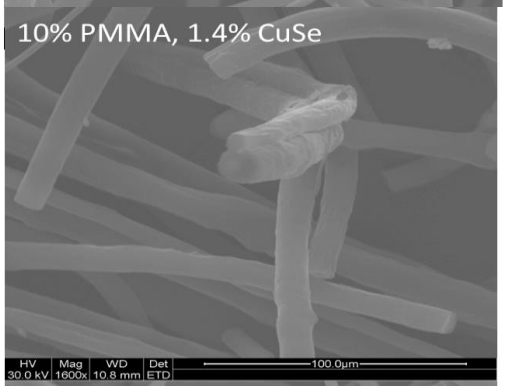
Sudden increased in conductivity at the 0.6% copper selenide polymer matrix which influenced the fibre formation.

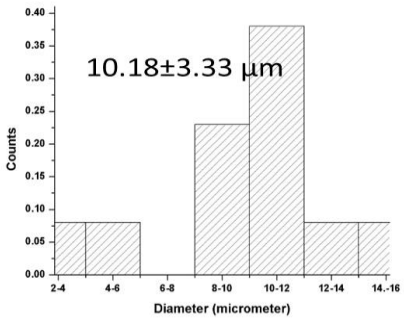


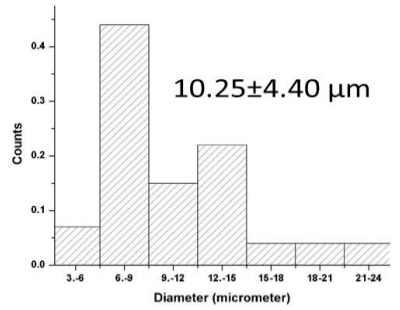






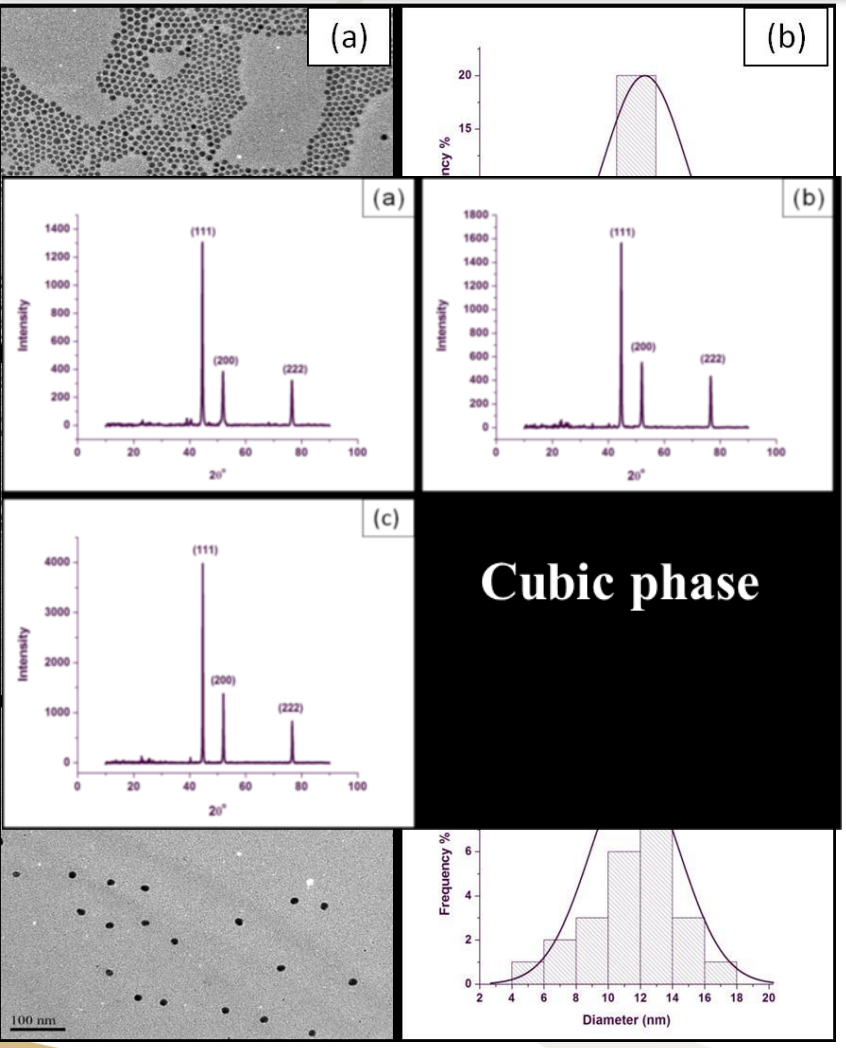




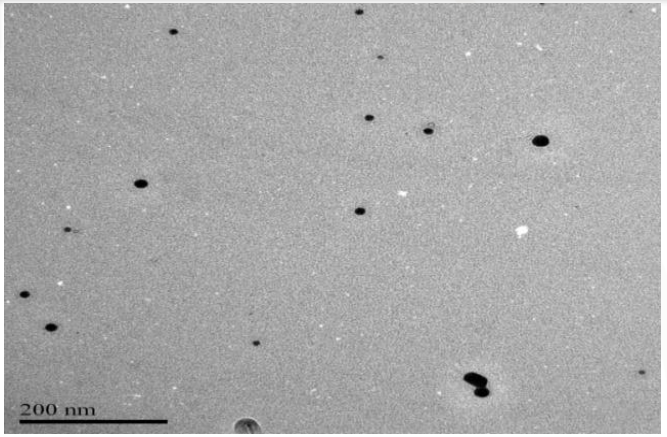


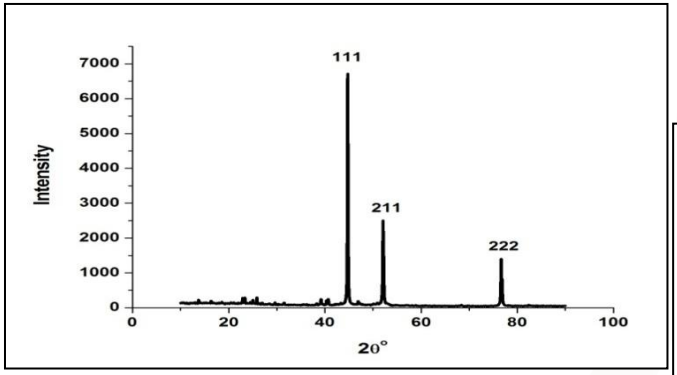
Ag_2Se/PVP Polymer fibers

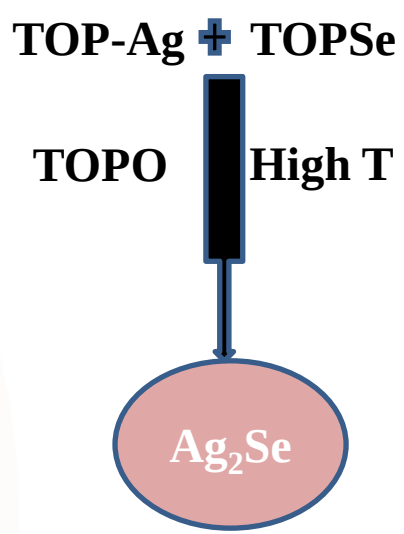
HDA-capped Ag_2Se nanoparticles: Temperature variation

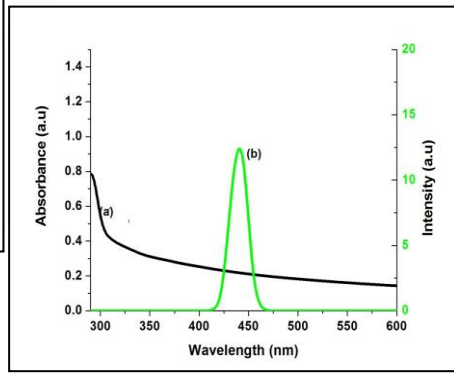


TOPO-capped Ag_2Se nanoparticles





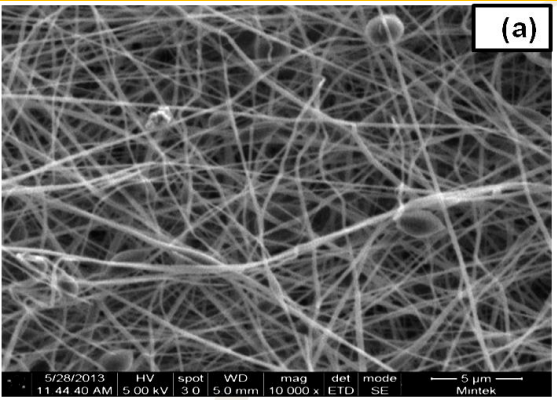


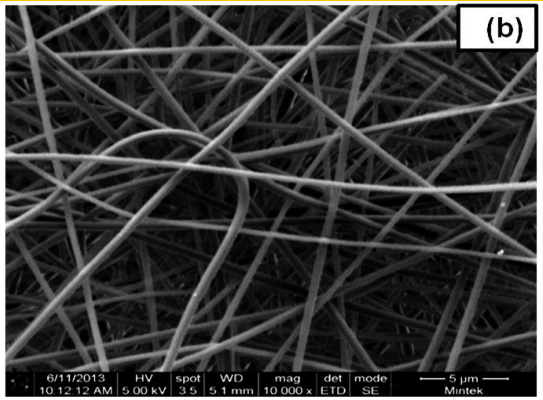


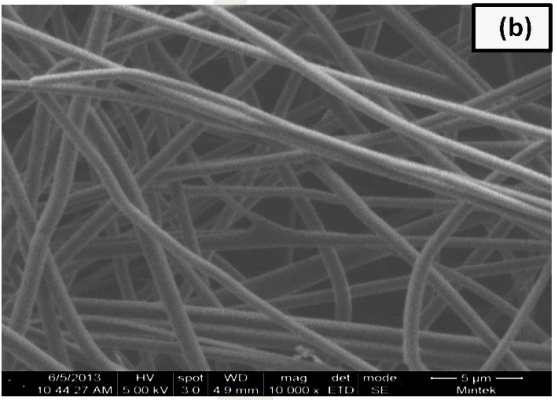
HDA-capping agent producing better yield and effective homogeneity of particle sizes

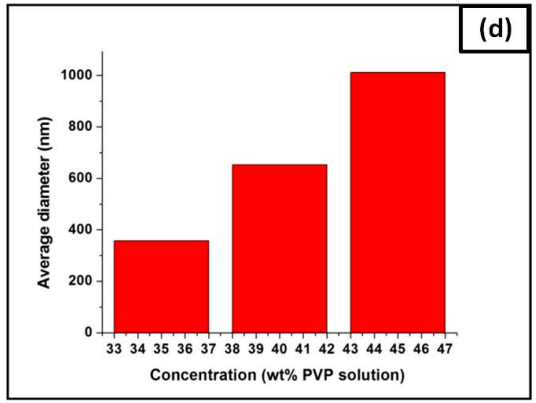
DS More, MJ Moloto, N Moloto, Chalcogenide Letters, 2016, 13(5), 233-238

Ag_2Se/PVP Fibers



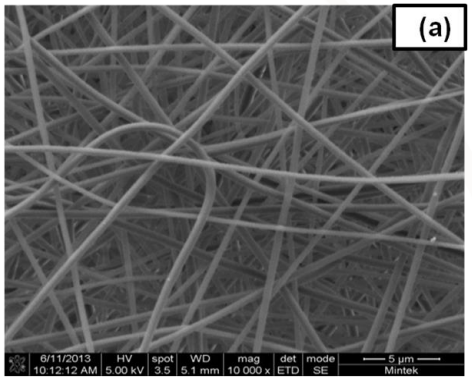


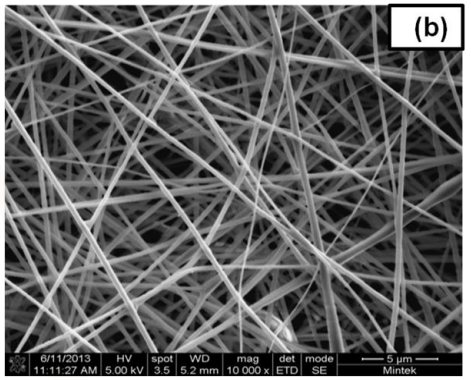


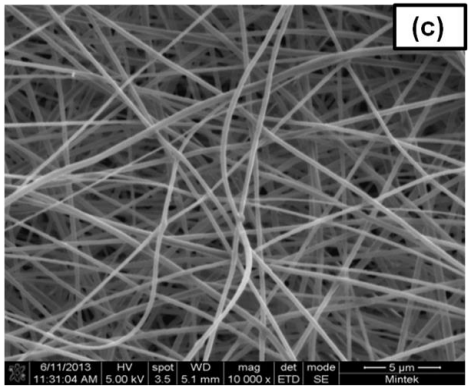


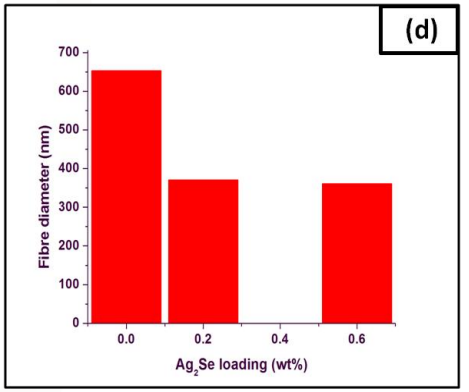
SEM images of different PVP concentrations (a) 35wt%, (b) 40wt% and (c) 45wt%

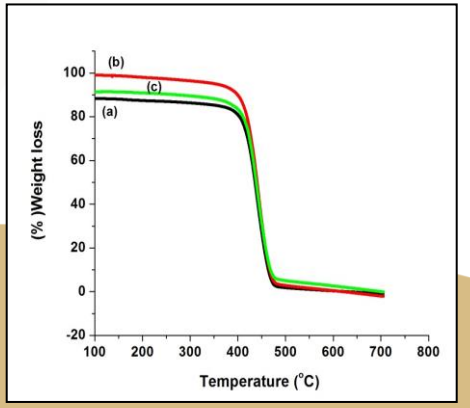
SEM images of (a) PVP-40wt%, (b) 0.2wt%, (c) 0.6wt% Ag_2Se/PVP composite fibres







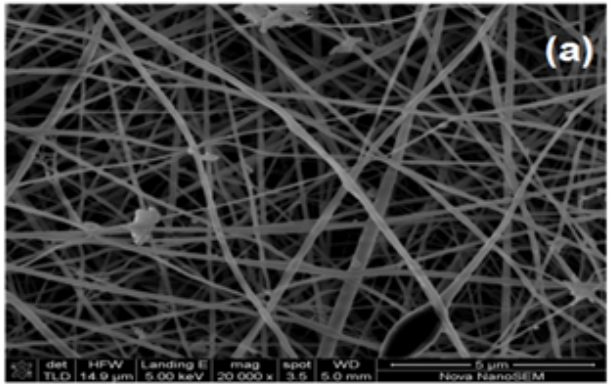


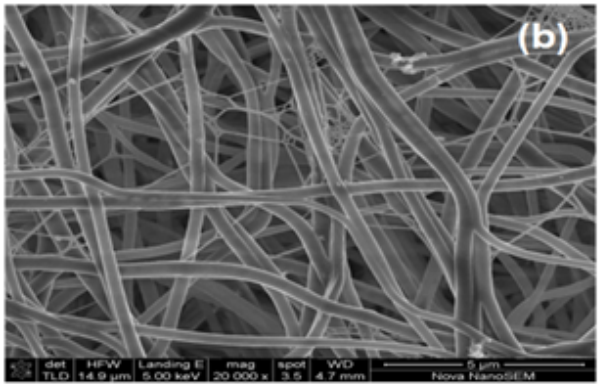


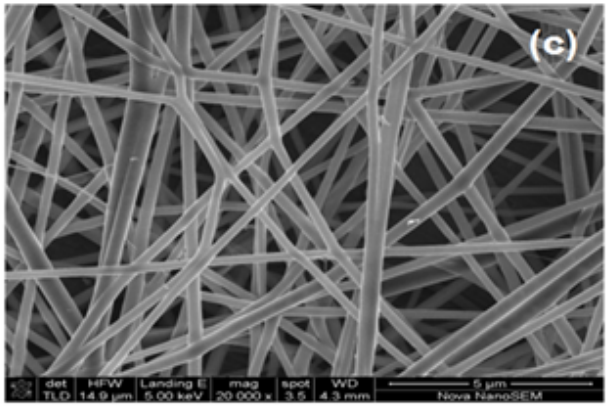
DS More, MJ Moloto, N Moloto, KP Matabola, Ag_2Se: Materials Research Bulletin, 2014

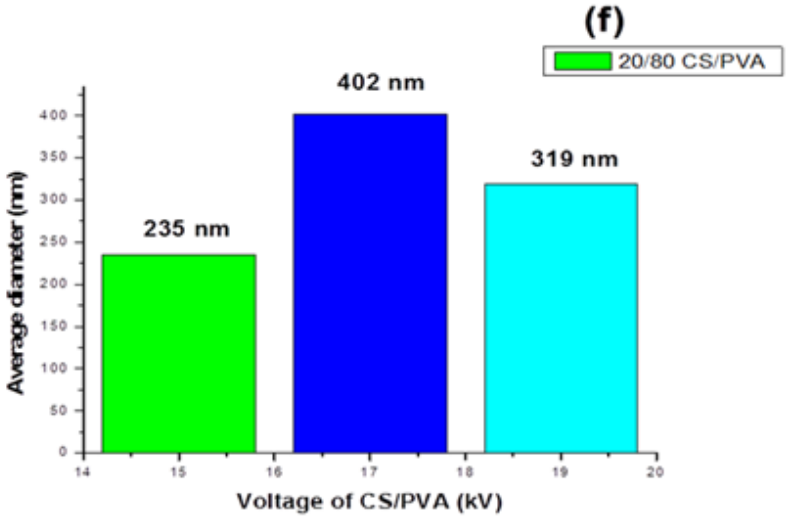
Polymer Blended fibres

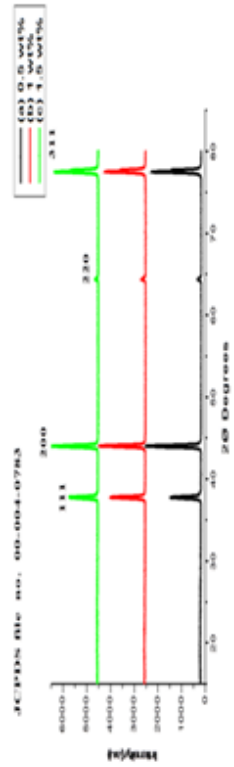
SEM images of CS/PVA blend weight ratio of 20/80 and fiber size distribution at different voltages (a) 15 kV, (b) 17 kV and (c) 19 kV with distance of 15 cm.







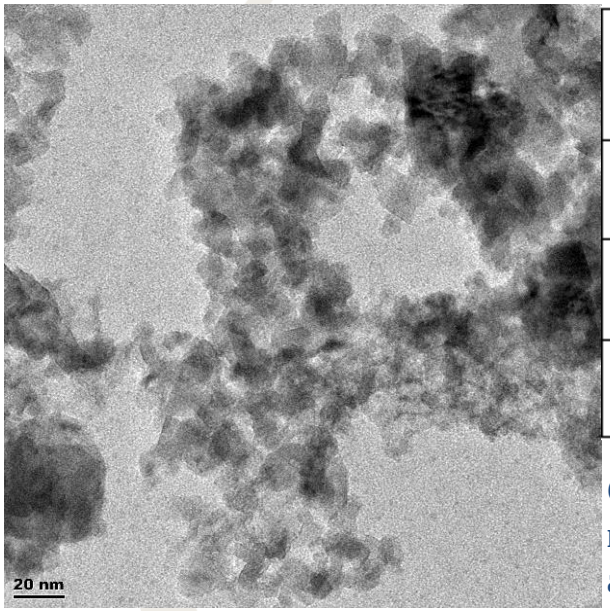




Increment of voltage improved the fibres uniformity and increases the charge density which ultimately favoured narrowing the average fibre diameter.

TiO_2 / CA/ PAN Polymer fibers

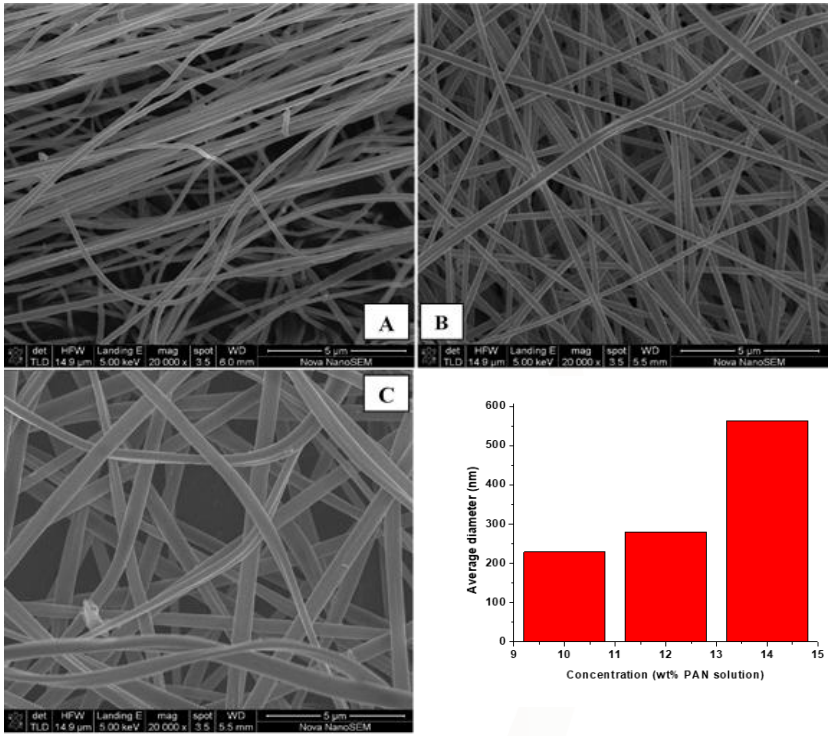
TiO_2 nanoparticles embedded on the polymers, Cellulose Acetate and Polyacrylonitrile



TEM image of TiO_2 nanoparticles prepared at calcination temperatures 500 °C.

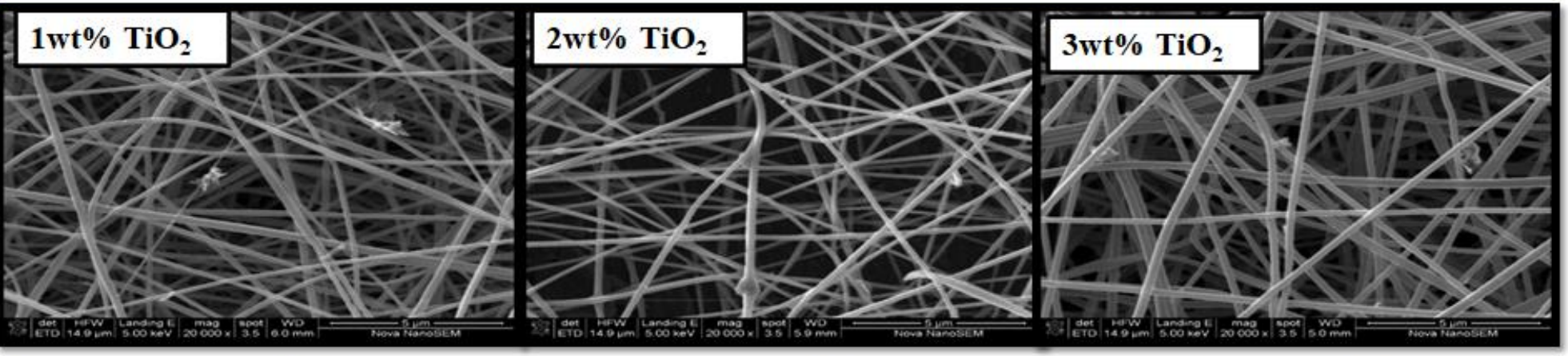
Sample ID	Crystallite size (D) nm
TiO_2 at 400°C	5.51mn
TiO_2 at 500°C	5.82nm
TiO_2 at 600°C	6.49nm

Crystallite size of TiO_2 nanoparticles prepared at different calcination temperatures (a) 400 °C (b) 500 °C (c) 600 °C..



SEM images and average fiber distribution of PAN nanofibers at different polymer concentrations (a) 10wt%, (b) 12wt% and (c) 14wt%.

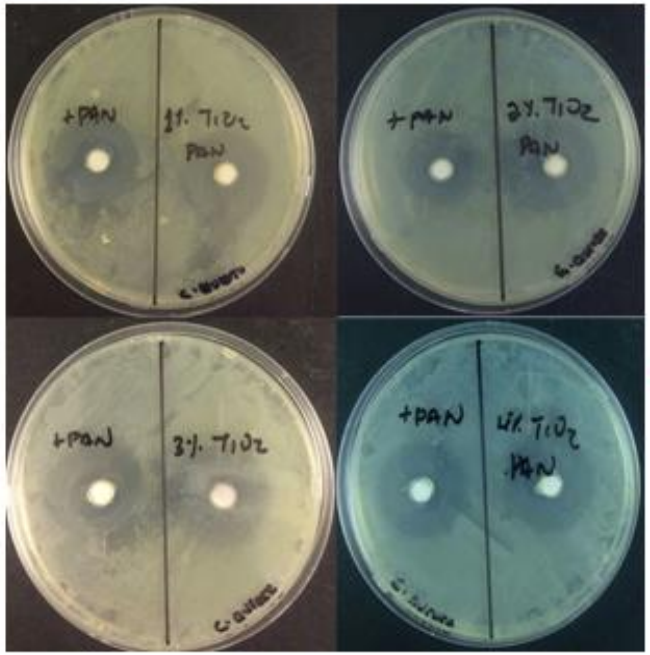
Effect of TiO_2 nanoparticles Loading



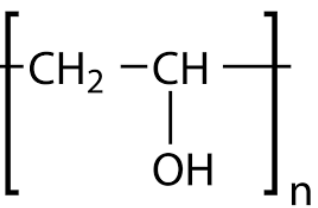
Average diameter: 177.84nm **Average diameter: 181.12nm** **Average diameter: 259.36nm**

Average diameter increases with increasing nanoparticles addition

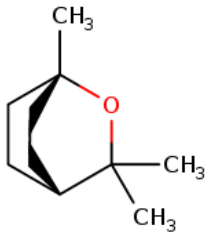
The presence of TiO_2 nanoparticles in the polymer was found to be strongly affecting the electrospun nanofibers antimicrobial activity. PAN/TiO_2 nanofibers were effective against all tested microbes.



- **The antimicrobial activity of PAN/TiO_2 increases with the increasing load of TiO_2 nanoparticles.**
- **E. coli was the most sensitive microbe and S. aureus was the least sensitive microbe against PAN/TiO_2 antimicrobial agents.**

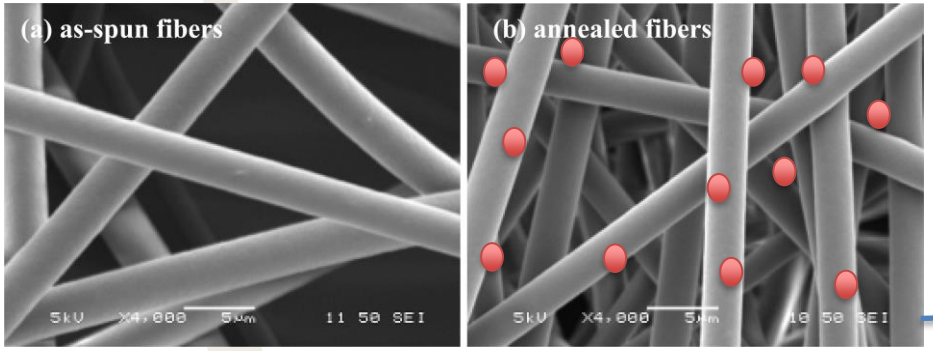


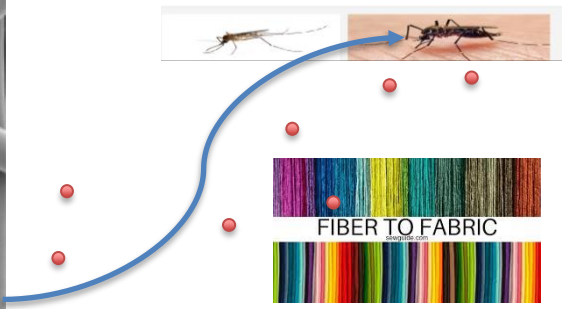
Fibers for mosquito repellants

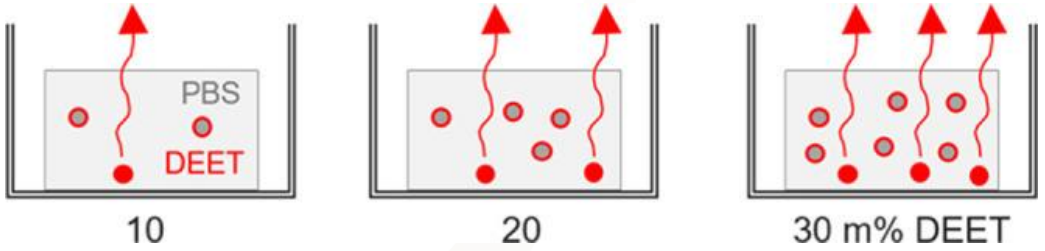


Incorporation of Eucalyptol into PVA nanofibers – potential mosquito repellent

Eucalyptol or DEET Slowly released to repel or kill Mosquitoes







Cloth head, leg and wristbands

Hande Ece Yener, Rafael Erdmann, Katalee Jariyavidyanont, António B. Mapossa, Walter W. Focke, Georg Hillrichs, and René Androsch; *ACS Omega* **2022** *7* (10), 8377-8384; DOI: 10.1021/acsomega.1c05897

Fibers for wound healing

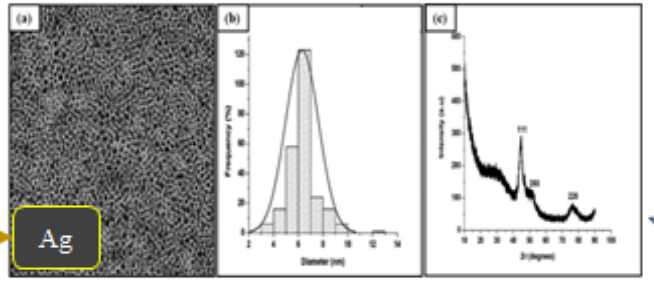
Precursors

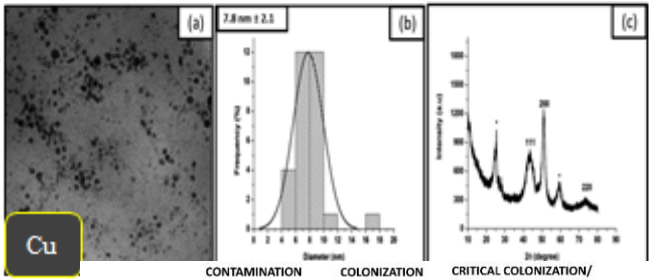
$AgNO_3$

Heated at 180 °C in oleylamine

Cu(Ox)

Nanoparticles



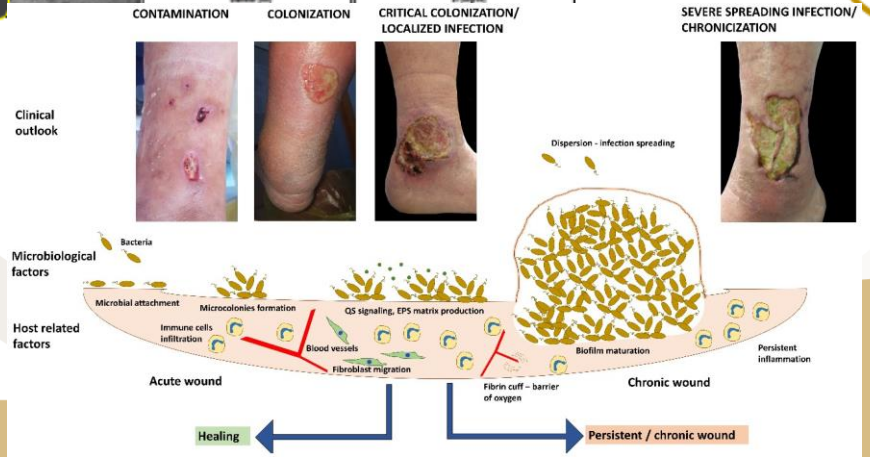


Polymer composite fibres

Chitosan/PVA

Ratios of 20:80' 30:70' 40:60 & 50:50
Voltage varied from15 to 25 kV

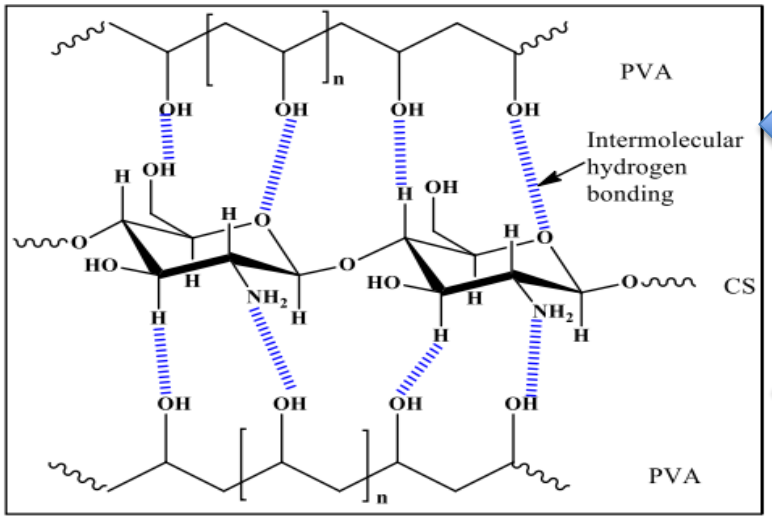
Added into polymer in 0,1 to 0,4wt%



Chronic wounds complications

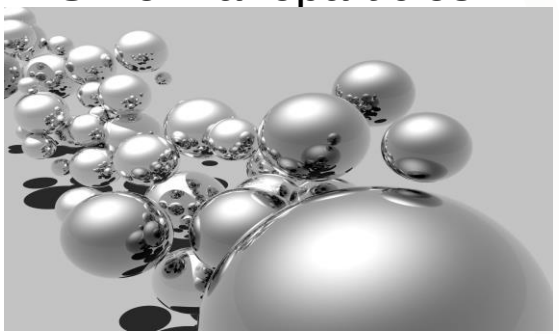
Fibers for Slow Release of plant extracts

Alkaloids, Flavonoids, Phenols – GC-MS



Plant extracts

Silver nanoparticles

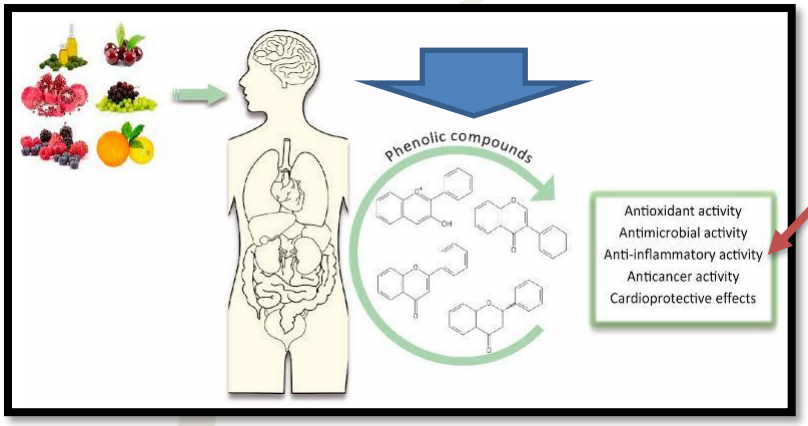


On-Going Project with VUT and the University of Masaai Mara in Kenya

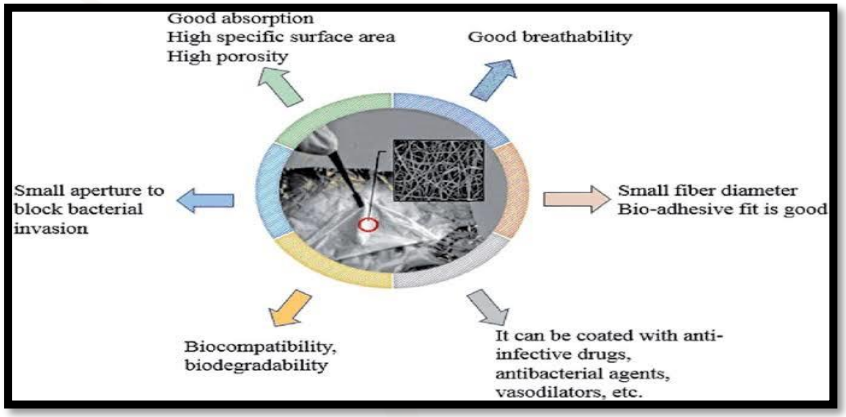
Bean Weavil infestation

Mould in bean packaging bags

Plant Extracts

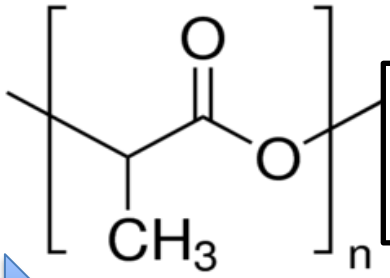


Antimicrobial



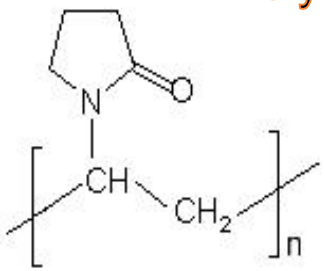
P. Alchemilloides **contains phenolic compounds**

Alkaloids, Flavonoids, Phenols – GC-MS

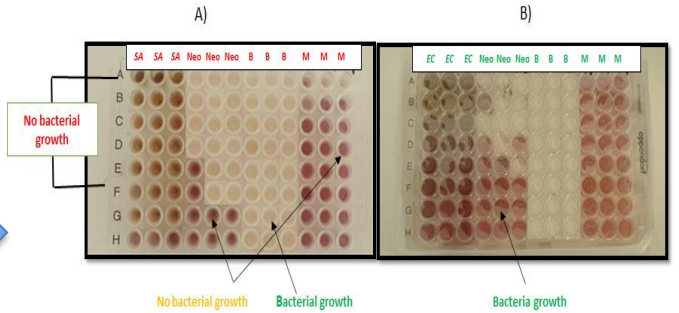


CA has good hydrophilicity nature

Polymer Blended Fibers



PVP is approved by FDA



Showed Moderate Antibacterial properties. MIC values for *staphylococcus. aureus* = 0.156 & *E. coli* = 2.50

THE FUTURE IS IN RECYCLING

- Accumulation of new materials or technologies result in excessive supply of dormant materials such that the next best approach is to find alternative uses of the same new materials or devices used for solving current societal problems.
- The Future is Finding New uses for Recycled or Newly Developed materials or Technologies.

A Group of Students from Wits and VUT in 2017

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Postdoctoral fellows: Dr. Mbali Sibiya-Mahlambi, Dr. Pardon Nyamukamba, Dr. Pierre Mubiayi, Dr. Wesley Omwoyo, Dr. Mildred Airo

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Dr Phillemon Matabola, Mintek

Dr Andrew de Vries – Digital Economy at the Innovation Hub

Prof James Darkwa

Prof Nosipho Moloto, WITS School of Chemistry

UNIVERSITY OF ZULULAND

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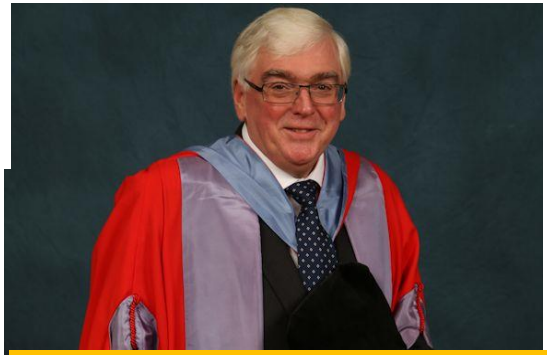
Prof Neerish Revaprasadu

MANCHESTER 1824

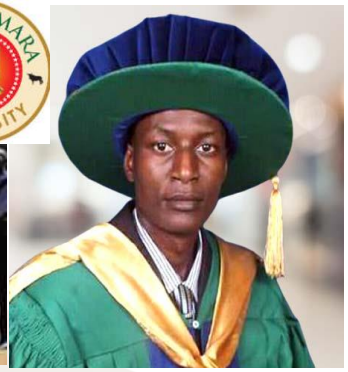
The University of Manchester



Paul O'Brien

CBE FRS FREng FRSC

Passed away in 2018



Collaborative Team at the University of Maasai Mara in Kenya led by Dr Wesley Omwoyo

Dr Samkeliso Takaidza

Dr Elvera Viljoen

Dr Nolutho Mkhumbeni

THANK YOU