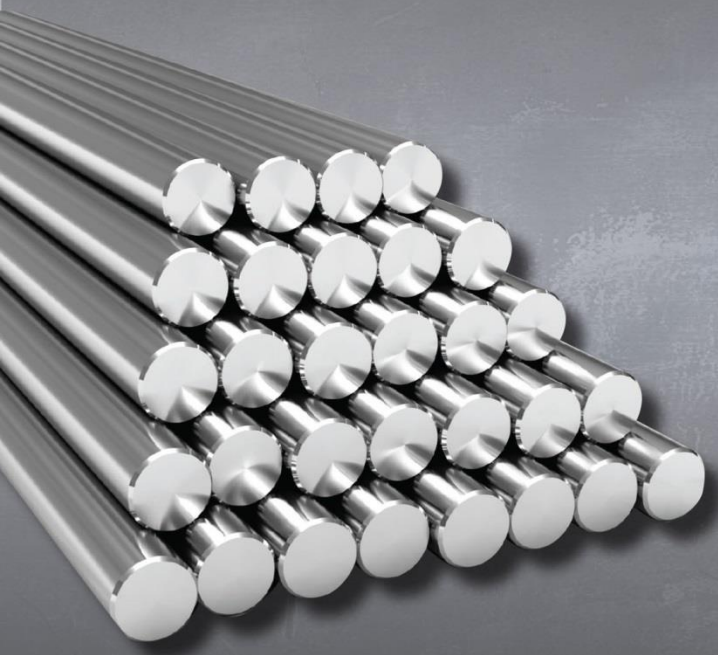
259th OMICS International Conferences

International Conference on

Smart Materials & Structures

June 15 -17, 2015 Las Vegas, USA



Exploring the Fusion of Intelligence with Materials

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Inorganic-organic hybrid based Smart Coatings



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Definition **Smart Coatings**

Coatings capable of performing some pre-determined function

Some Example of Smart Coatings

- Self Healing
- Self Cleaning
- Conductive
- Corrosion sensing
- Light sensing
- Photo catalytic

Self Cleaning

Coatings on which dust can be removed using some stimuli – may be water drop

- The action of water drop will depend upon whether the surface is hydrophobic or hydrophilic

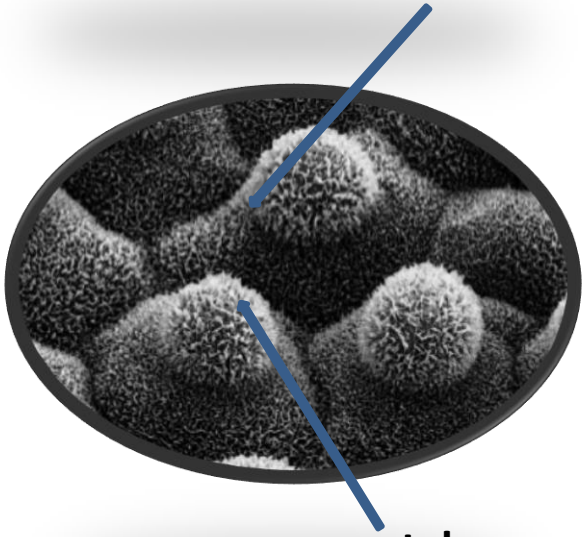
What is Superhydrophobicity?

- The ability of surfaces to make water bead off completely and thereby wash off contamination very effectively is called as “Lotus leaf effect”

- Macro – nano surface morphology & very low surface energy due to **Cuticular Wax** produces lotus effect on the surface



Roughness



Low energy –wax crystals

How to achieve Superhydrophobicity?



- **Lower Surface Energy:** $-CF_3 < -CF_2 < -CH_3 < -CH_2$
- **Surface Roughness:** Micro Nano Texturing *(C.A > 130)*



C.A < 90

C.A < 120

C.A > 150

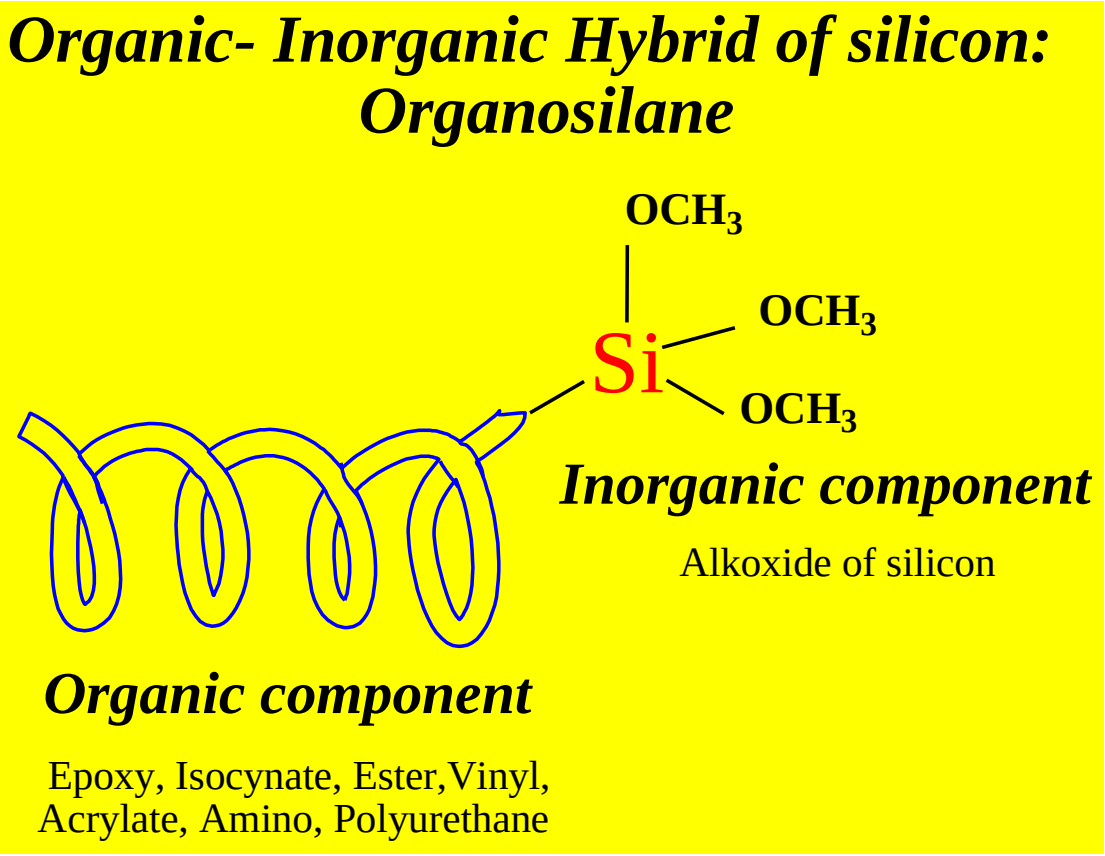
How to make a surface Hydrophobic ?

We followed three approaches :

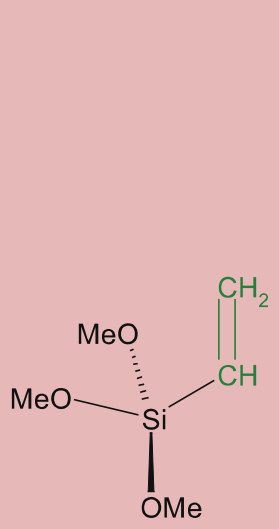
- Grafting with fluro-based polymers which saturate the surface with strong bonding
- Changing the surface roughness
  - By physically changing the surface roughness by various etching processes
  - By addition of nano particles
- A combination of fluropolymers and nano particles
- Non-fluro approach

Inorganic-Organic Hybrids

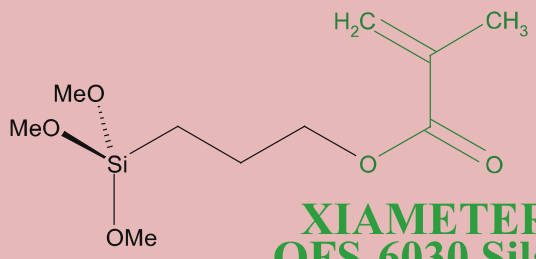
- Organic-inorganic hybrids are molecules containing a metal core bonded to reactive alkoxy groups and/or organic groups



Nomenclature of IOH



Dow Corning®
Z-6300 Silane

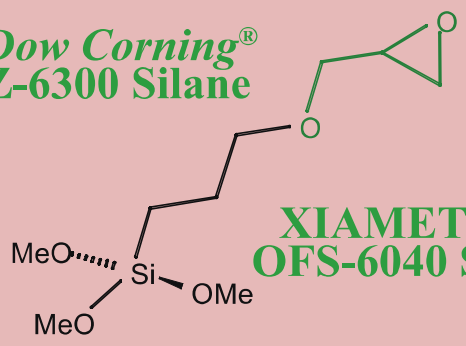


XIAMETER®
OFS-6030 Silane



OR'= methoxy, ethoxy or acetoxy

X= alkyl, aryl or organofunctional group



XIAMETER®
OFS-6040 Silane

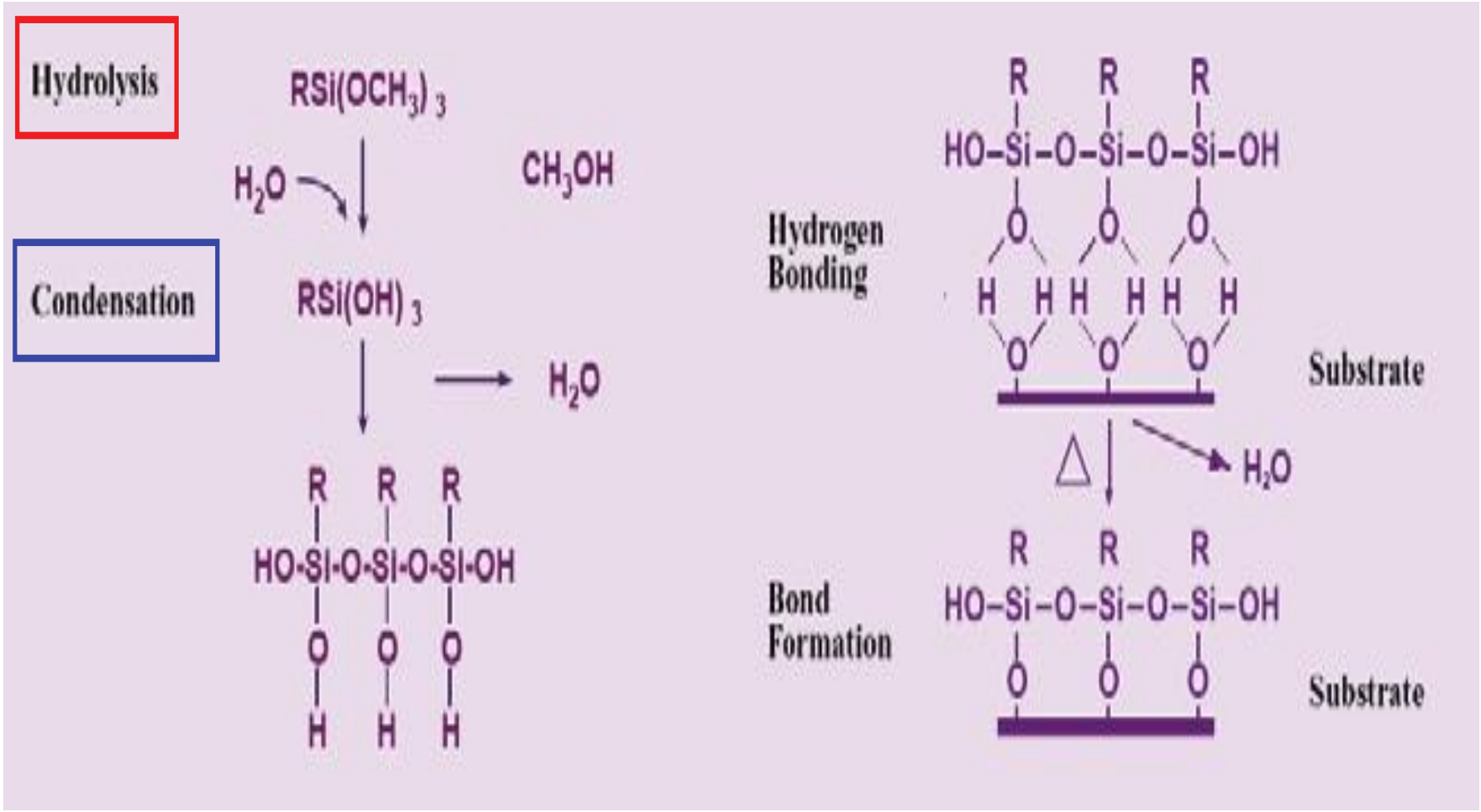


XIAMETER®
OFS-6341 Silane



Dow Corning®
Z-6011 Silane

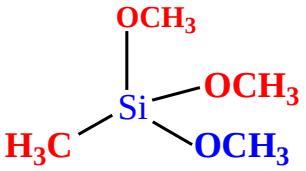
Advantage of Sol-Gel Process

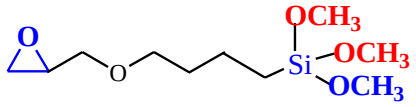


Sol-gel Coatings: The Work done at IITB

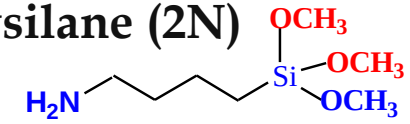
- Inorganic –organic Hybrid Coatings – having properties of both inorganic materials and organic materials

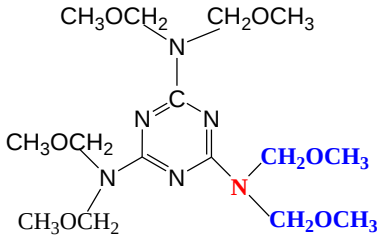
- **Precursors for coating formulation**

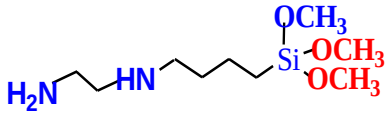




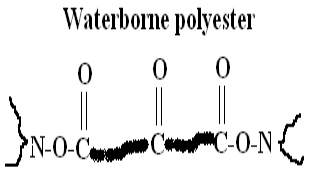
- **Methyltrimethoxysilane (MTMS)**
- **3-glycidoxypropyltrimethoxysilane(GPTMS)**
- **3-aminopropyltriethoxysilane (1N)**
- **N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (2N)**
- **Hexamethoxymethylmelamine (HMMM)**
- **Waterborne polyester(WPE)**
- **Waterborne alkyd(WKD)**

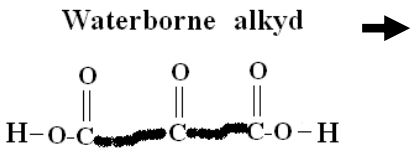




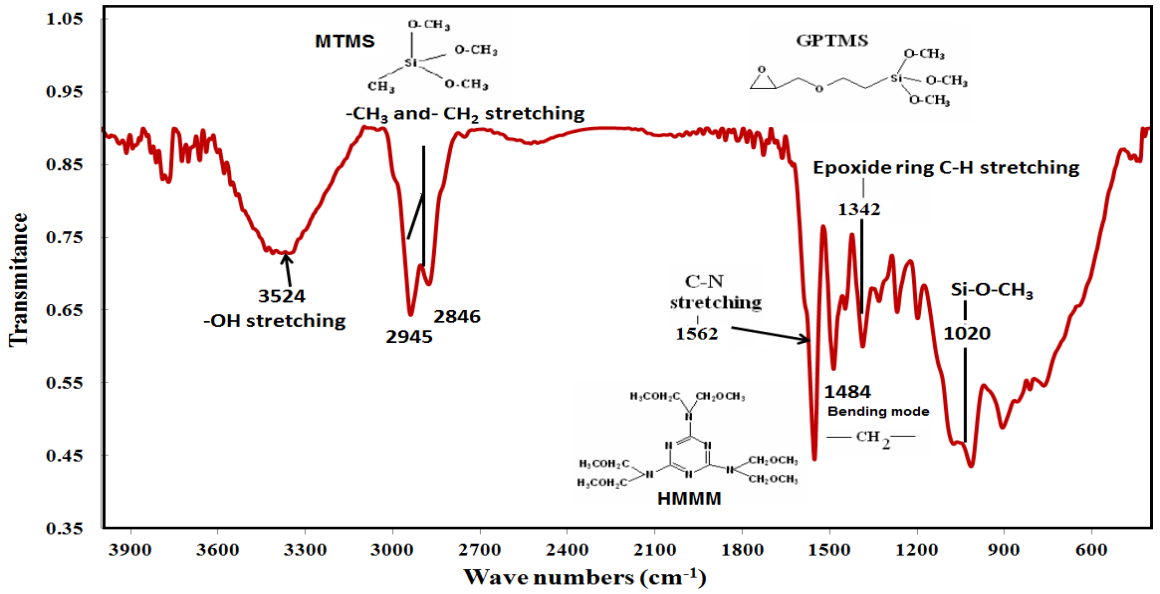


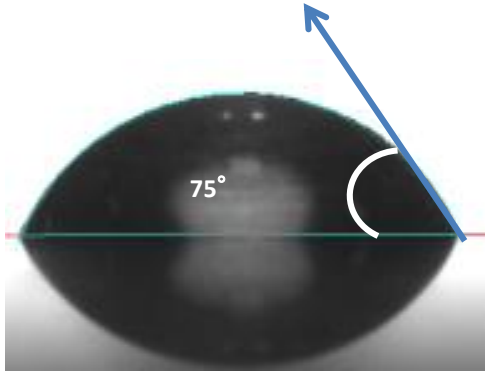
- **Coating formulations**
- **Epoxysilane coatings**
- **Polyester incorporated epoxysilane coatings**
- **Alkyd incorporated eposysilane coatings**

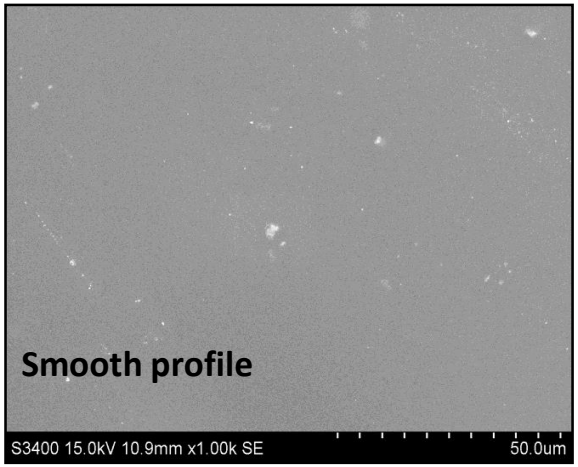


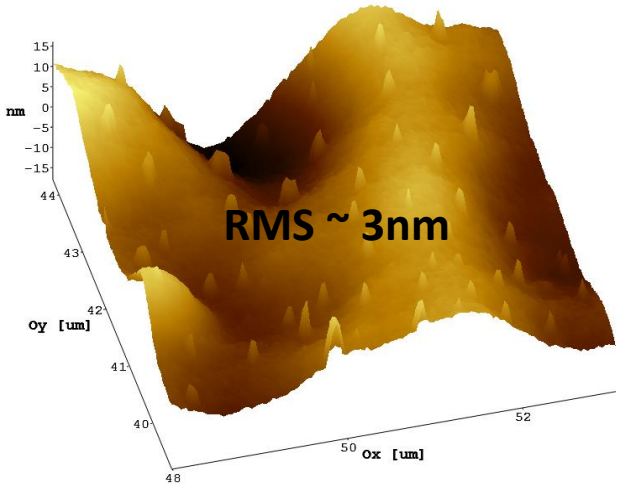


Characterization of Neat Sol gel





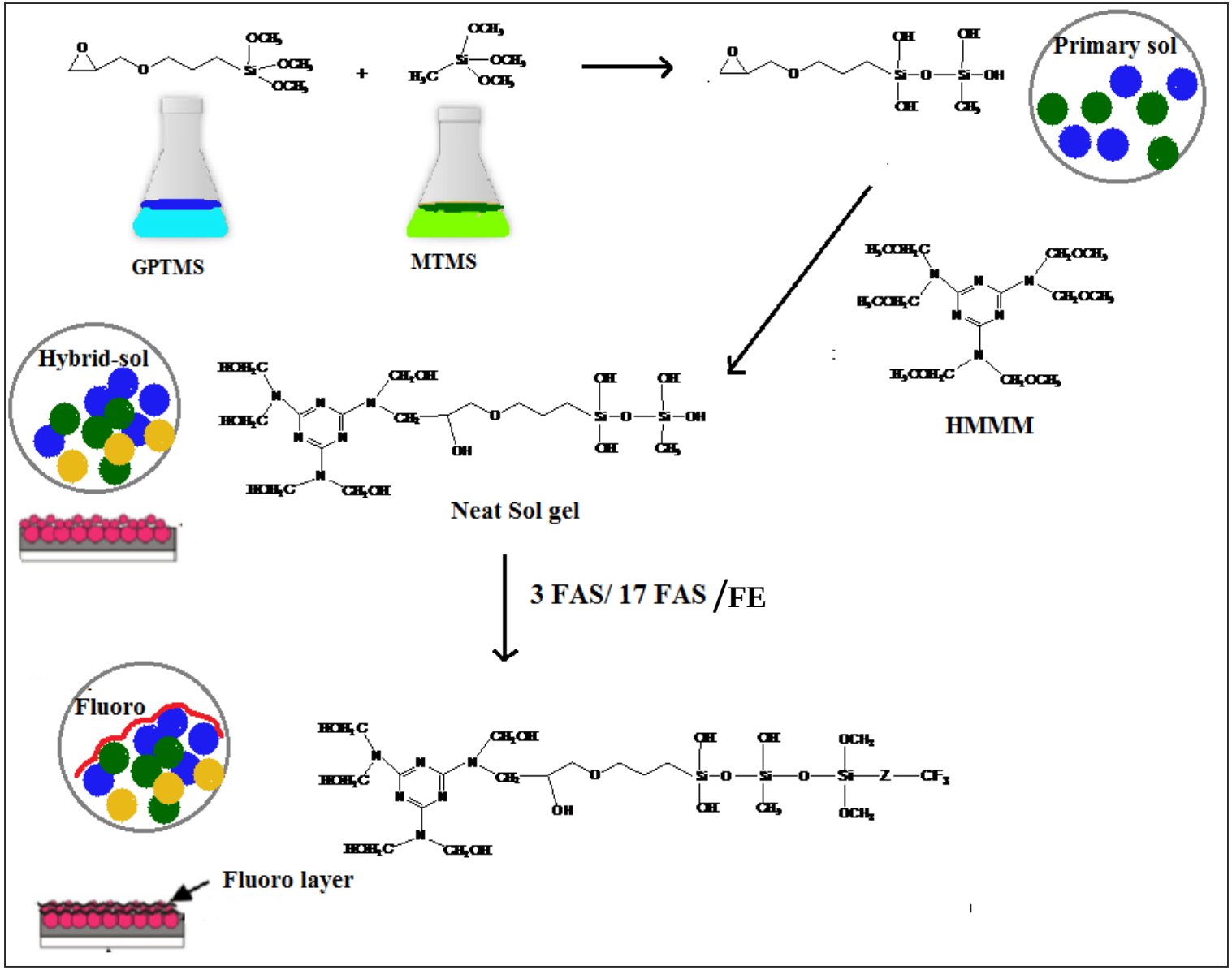




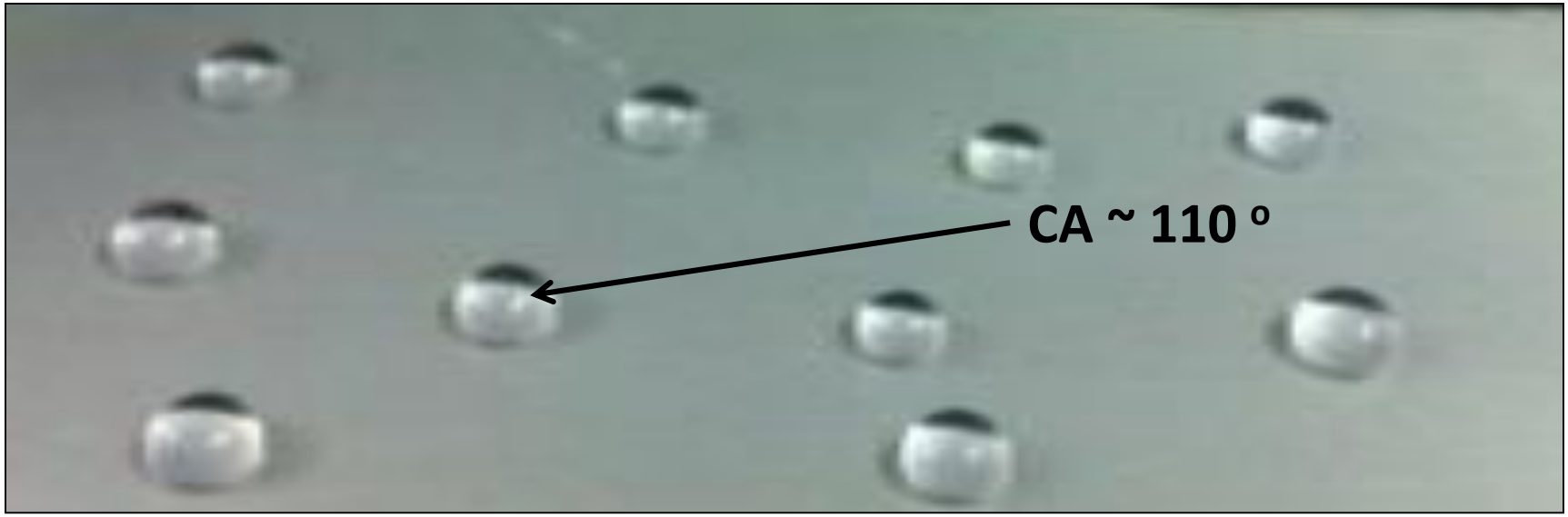
Fluro Approach

- 3, 3-Trifluropropyltrimethoxy silane
- Perflurodecyltrimethoxy silane (17 F atoms)
- Perflurodecyltrichlrosilane (17 F atoms0
- Short Chain C-6 atoms perfluro water based polymer (Commercial name Chemgaurd FEE-2000)

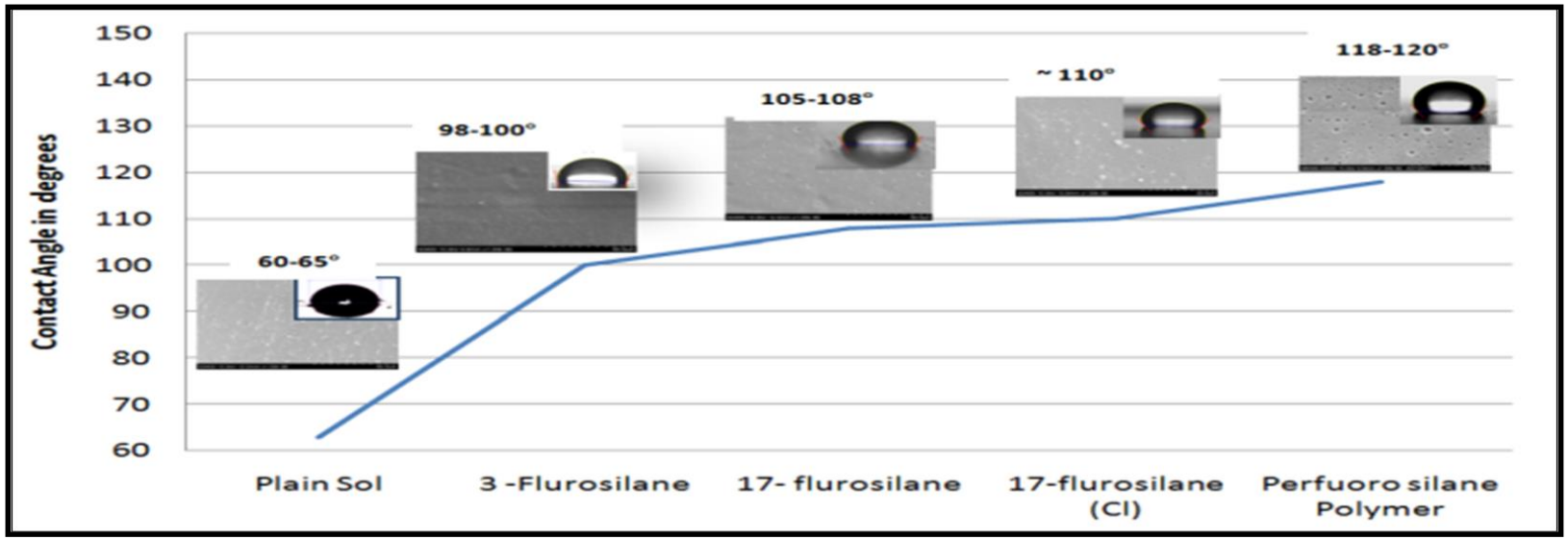
Synthesis of Fluoro-based sol-gel coatings



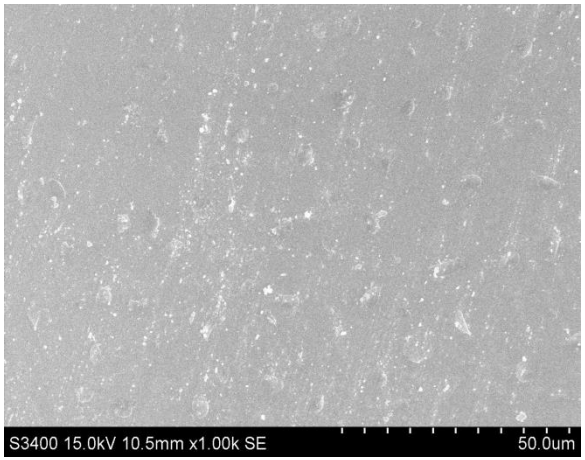
Aluminium



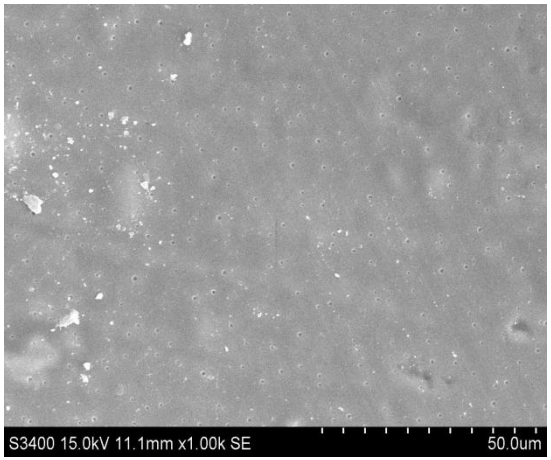
Comparison of various Fluoro-silanes



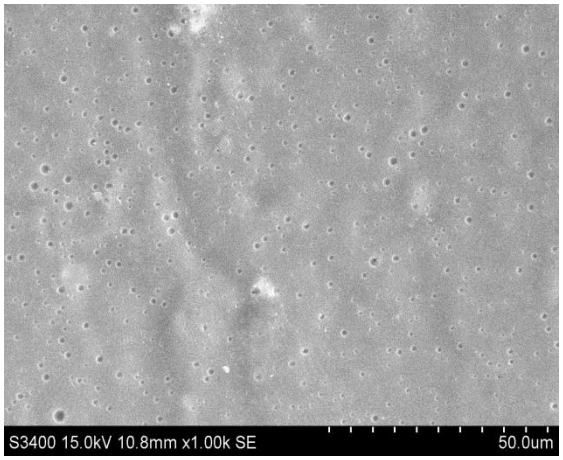
SEM micrograph of different wt% F.S. over aluminium



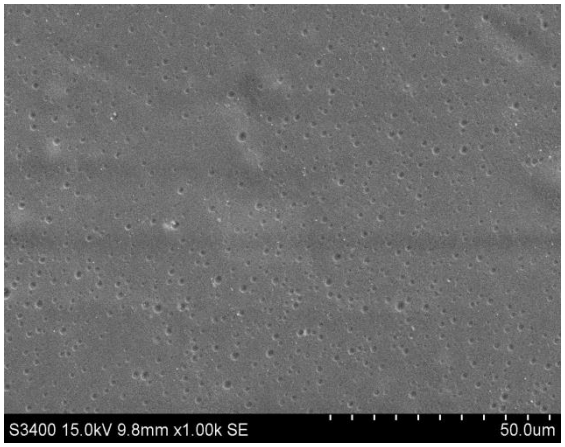
(a) 0.5 wt% F.S.



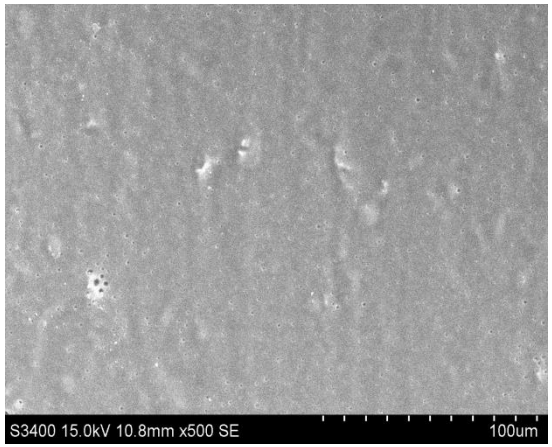
(b) 1wt%F.S.



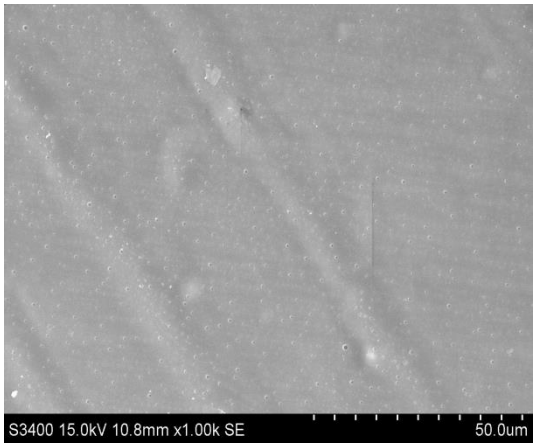
(c) 1.5wt% F.S.



(d) 2wt% F.S.

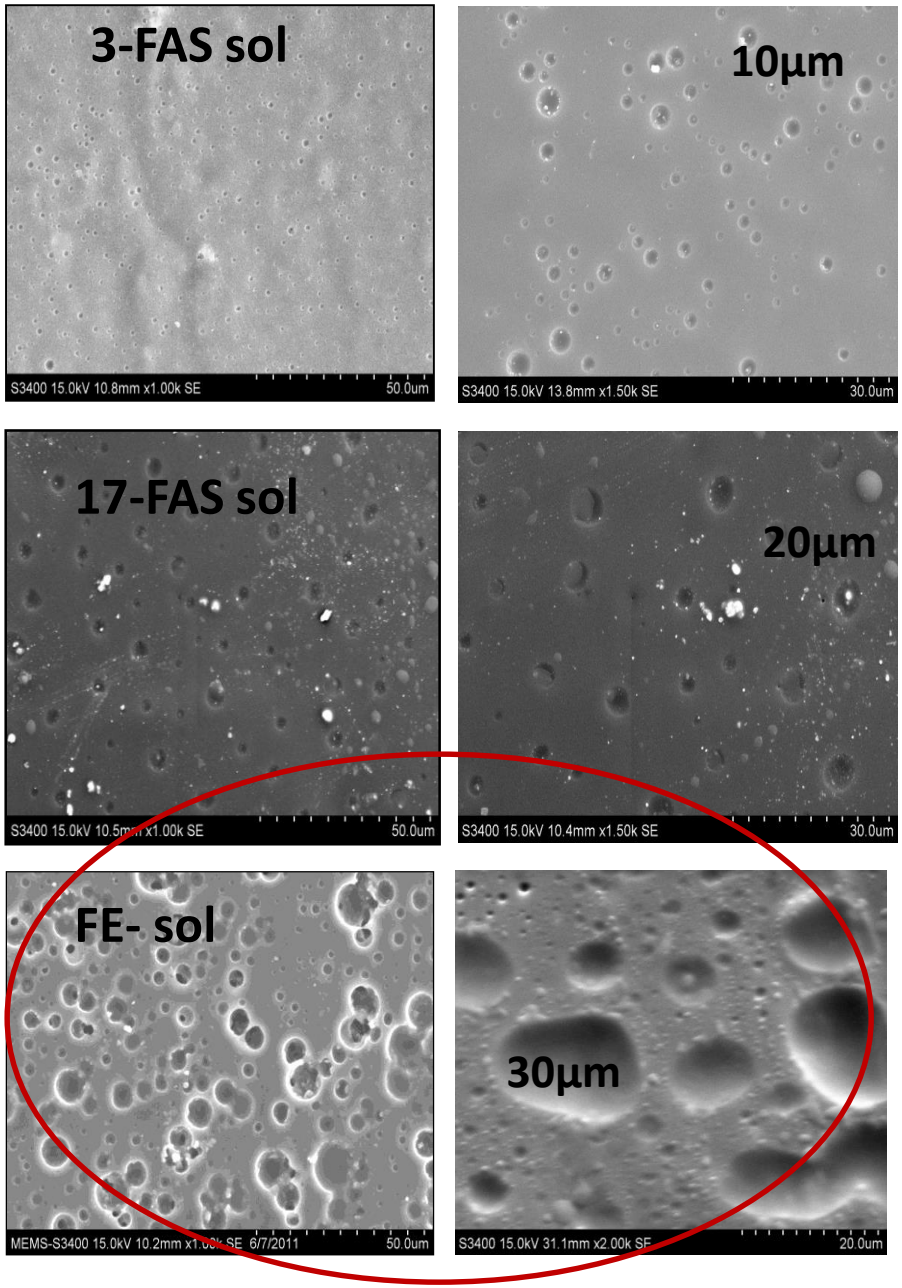


(e) 3wt%F.S.

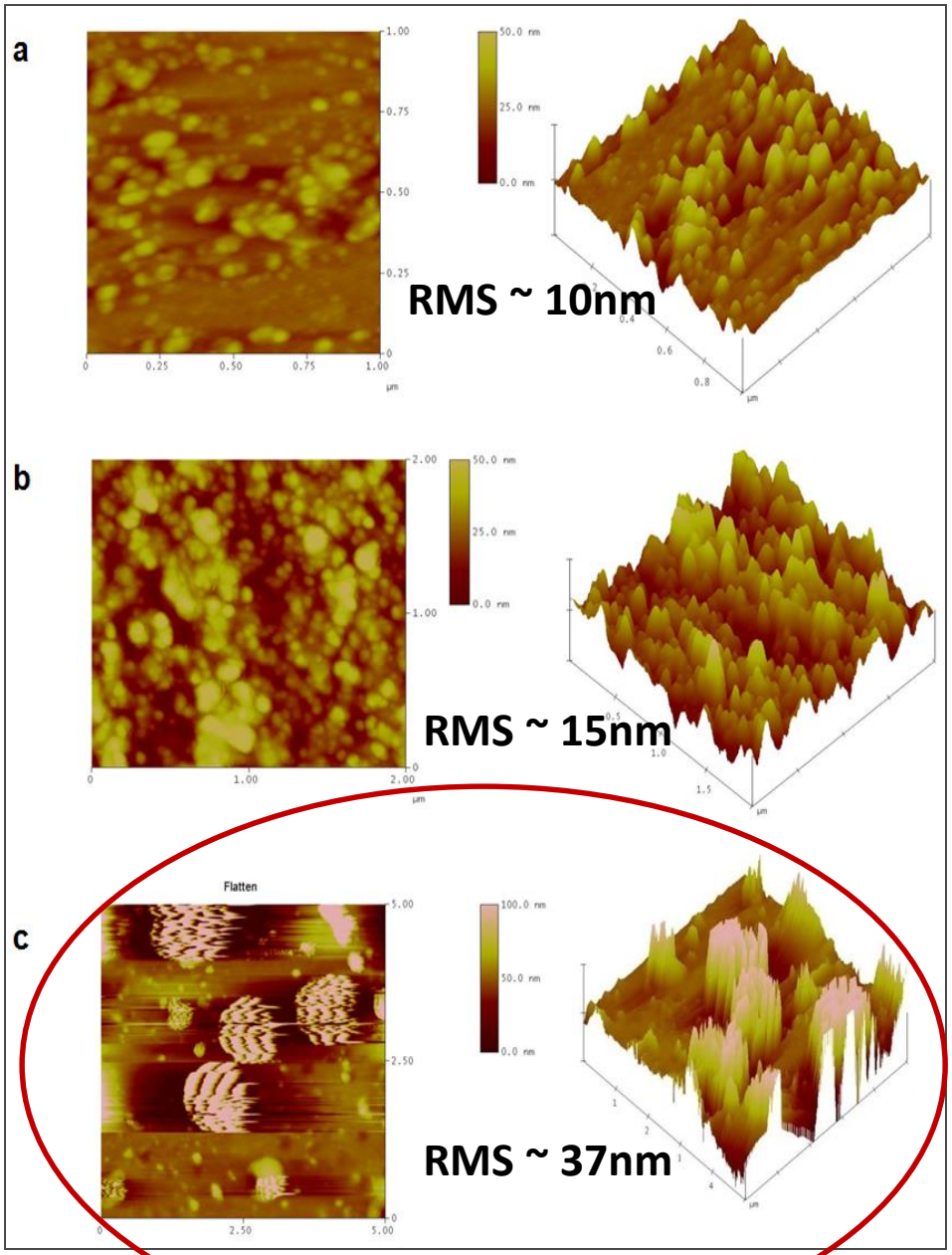


(f) 5wt%F.S.

Comparative SEM Analysis of various Fluorinated systems



Comparative AFM results of various fluoro modified sol-gel systems



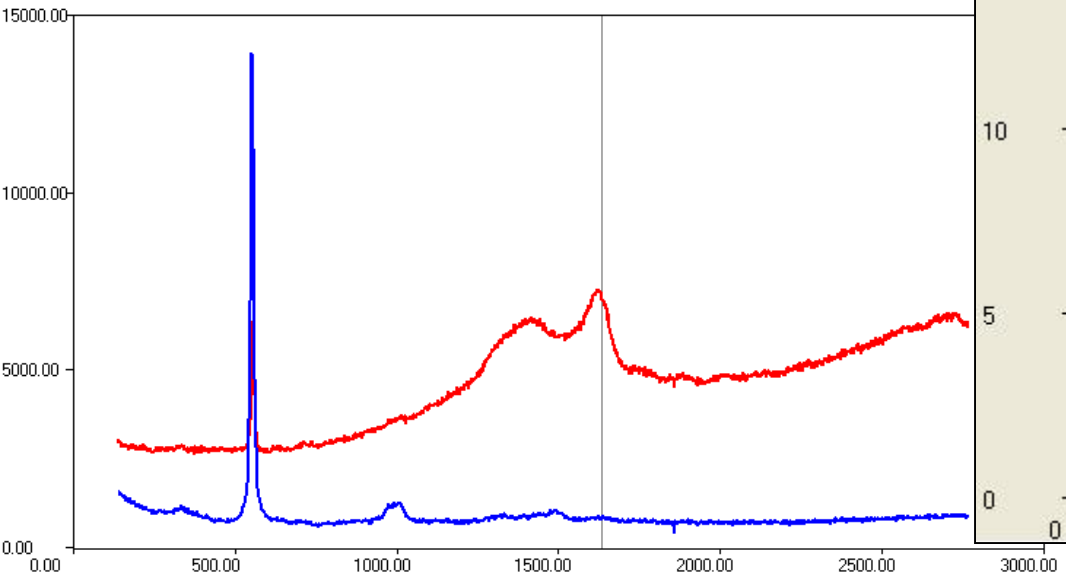
Role of Optimum Concentration

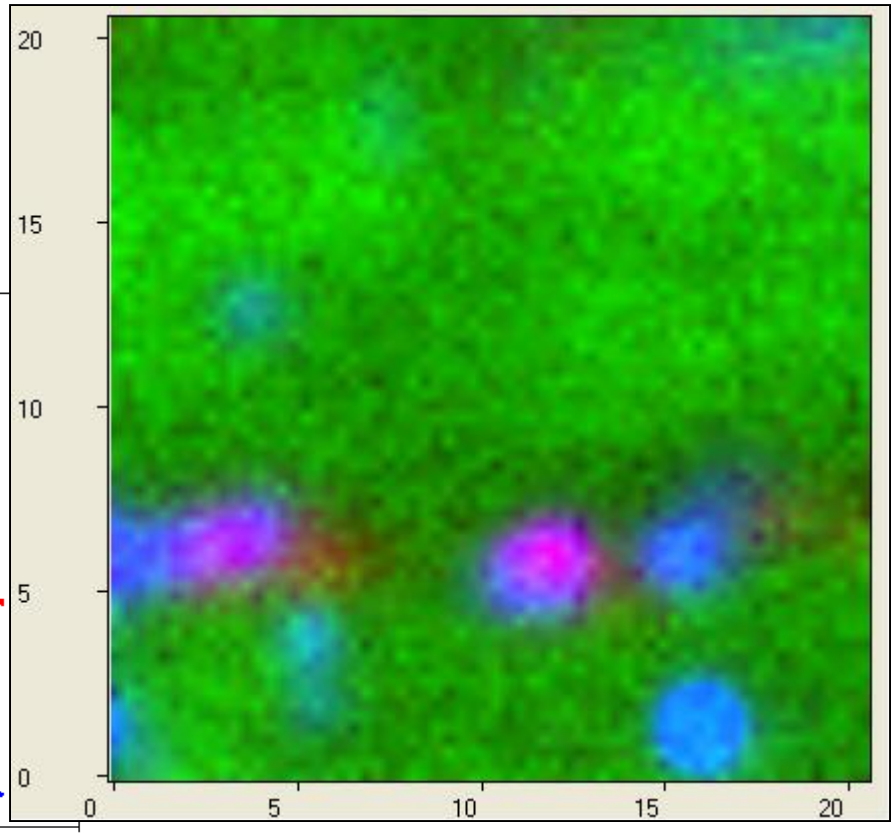
Both in the case of Fluro Addition and Nano-ZnO addition, it was found that there is optimum concentration at which :

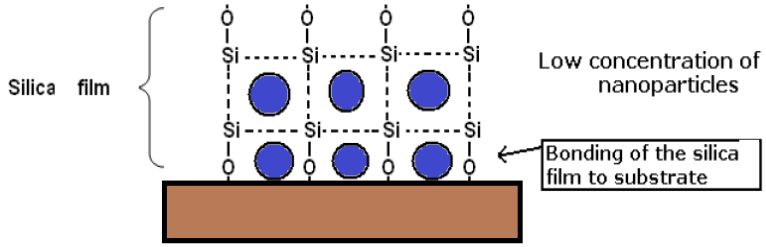
- We get maximum Contact angle
- Best Corrosion resistance
- Best Mechanical Properties
- Better UV blocking effect

AFM Analysis and Raman spectroscopy for FE-2000 emulsion + 2% nano ZnO

Raman spectral mapping







Green maps the 1455cm-1 sol Raman line

Blue maps silicon

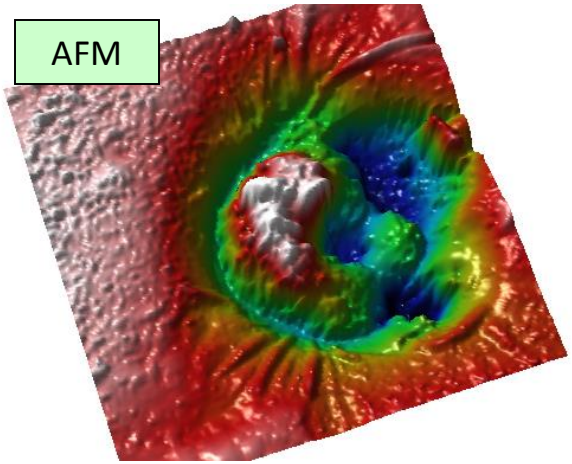
Red maps a fluorescent material containing amorphous carbon

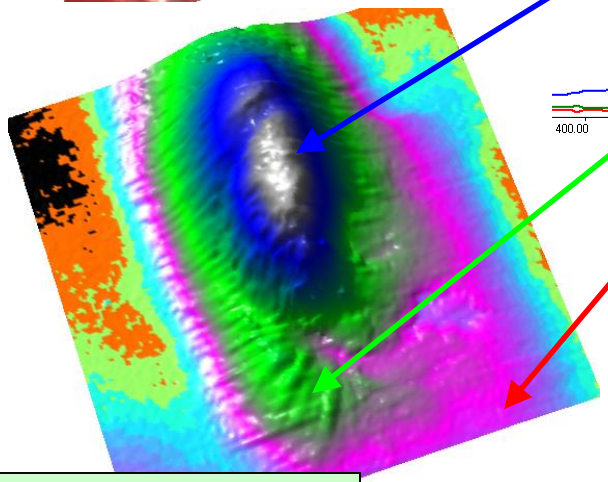
Spectra match mapping colour

AFM analysis and Raman Spectroscopy of FE200 + 4 %ZnO

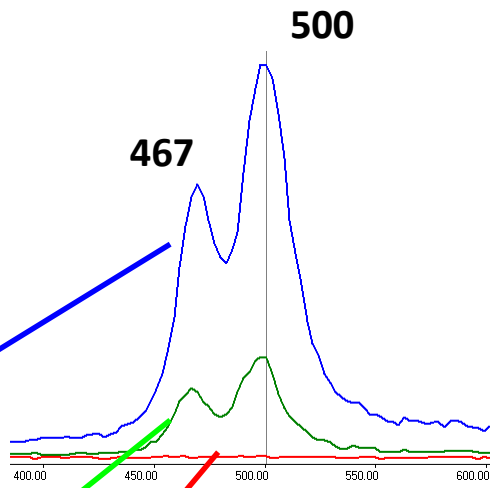
TERS AFM/Raman Map (8x8 µm, 100x100 points).
Side 20X0.42NA objective, Laser 671 nm, 0.05 mW, integration 0.2 sec.

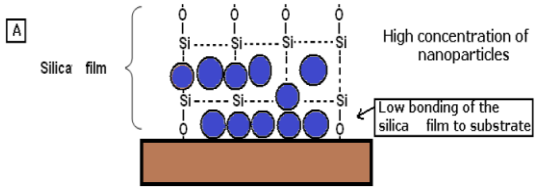
AFM

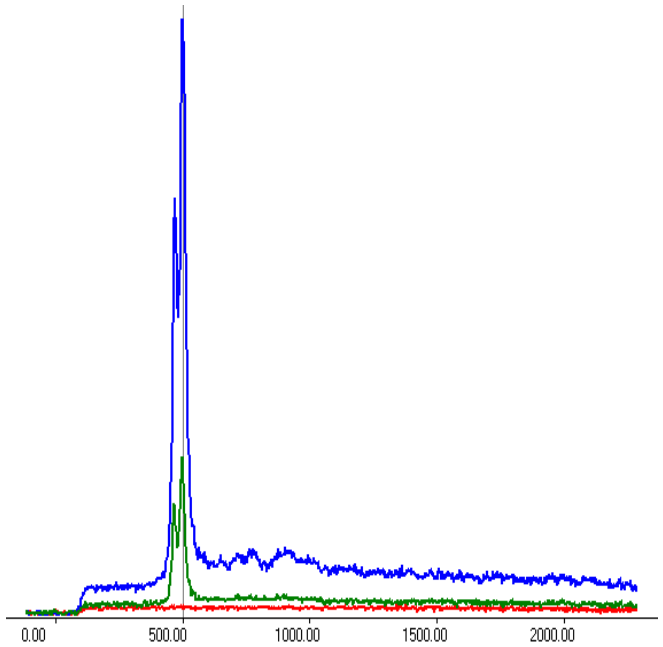




Raman 500 band Map



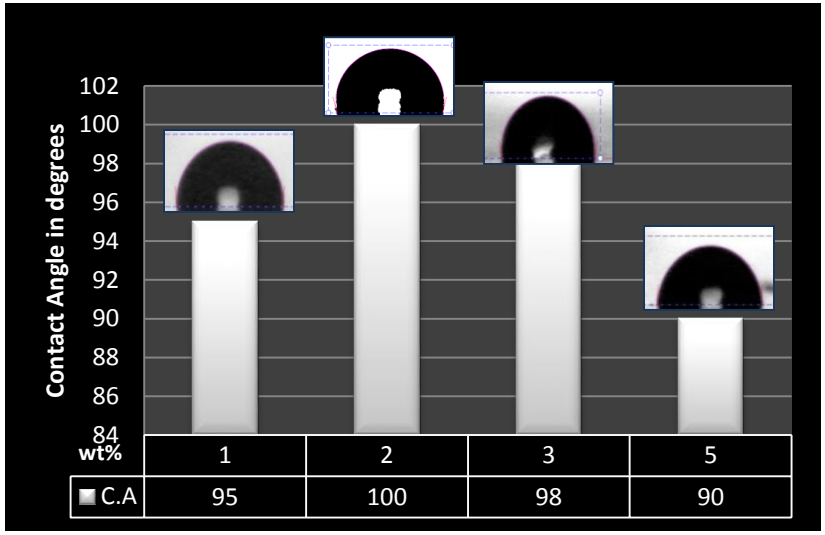


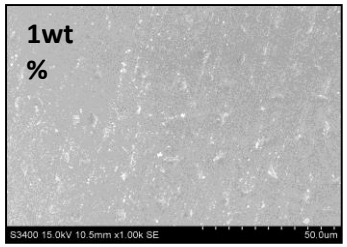


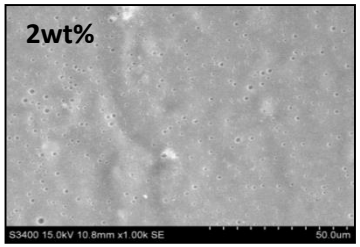
Raman spectrums from 3 different points.

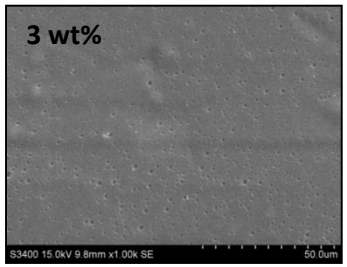
Map # 575

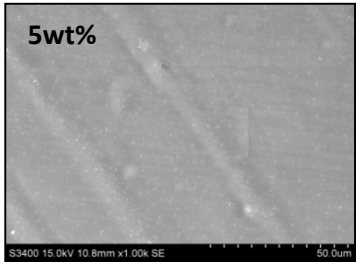
Effect of 3-Fluoro Silane









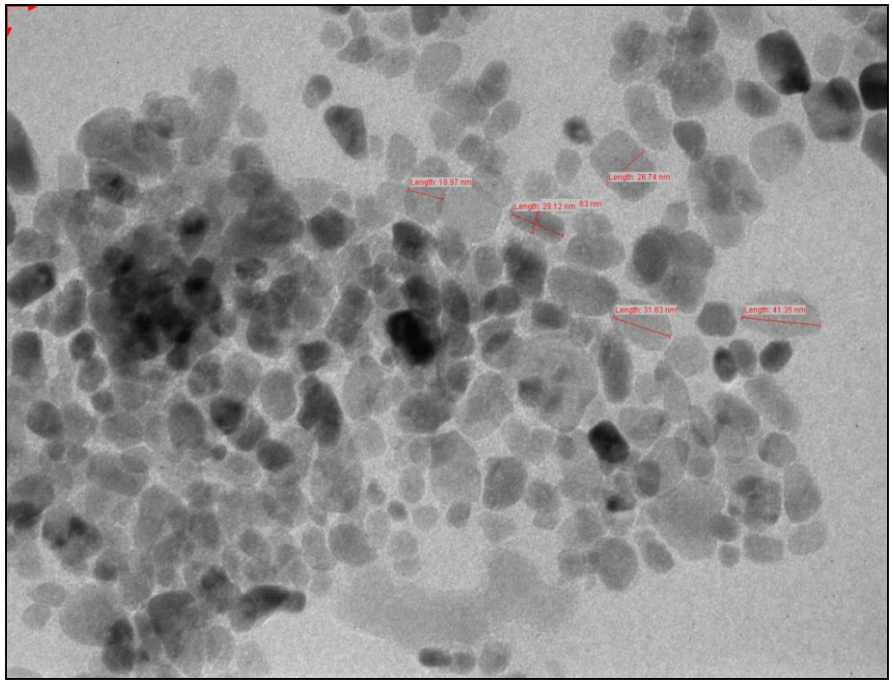


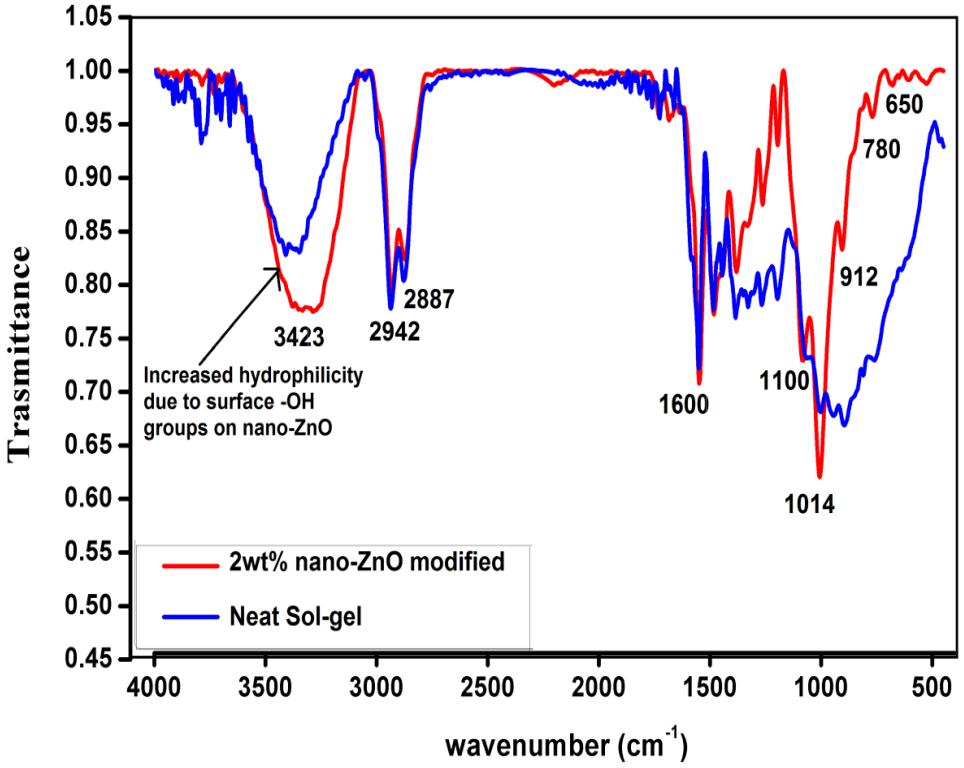
Wt% of fluorosilane	Percentage area removed	Cross-hatch adhesion Result on Al	Surface of cross-cut area
1	0%	5B	
2	0%	5B	
3	0%	5B	
5	0%	5B	

Wt% of fluorosilane	Pencil Hardness
1	4H
2	4H
3	4H
5	4H

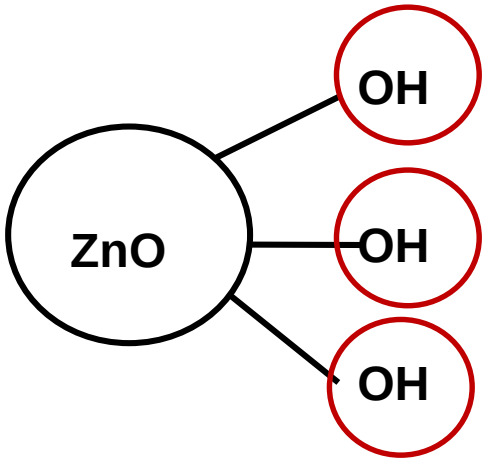
Effect of Nano Particles

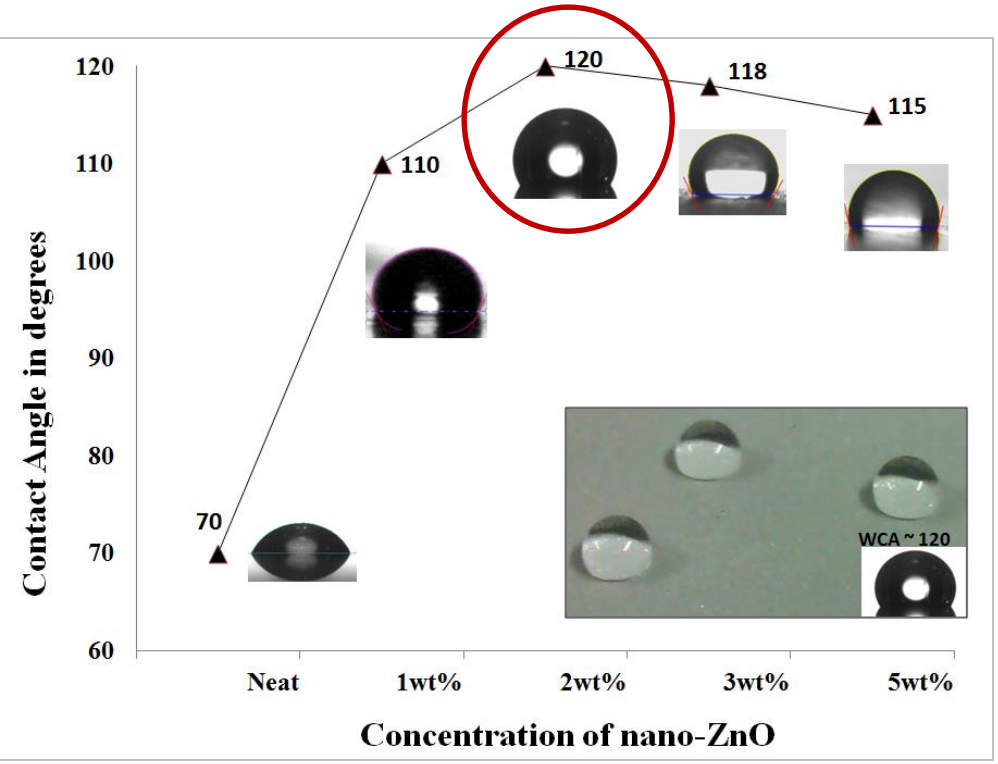
Modification of FE-sol with nano-ZnO particles

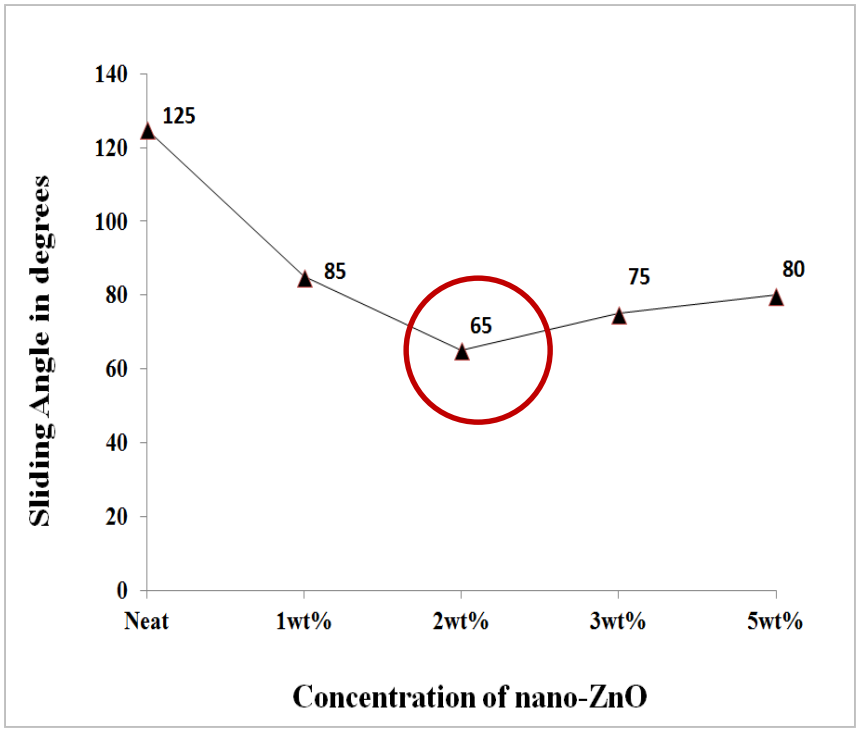




- Particle size - 30-40nm
- BET surface area - 45±20 m^2/g
- Hydrophillic surface hydroxyl groups- intense – OH peak in FTIR spectrum
- High tendency to agglomerate due to particle – particle interaction resulting in secondary and tertiary structures-low surface to volume ratio

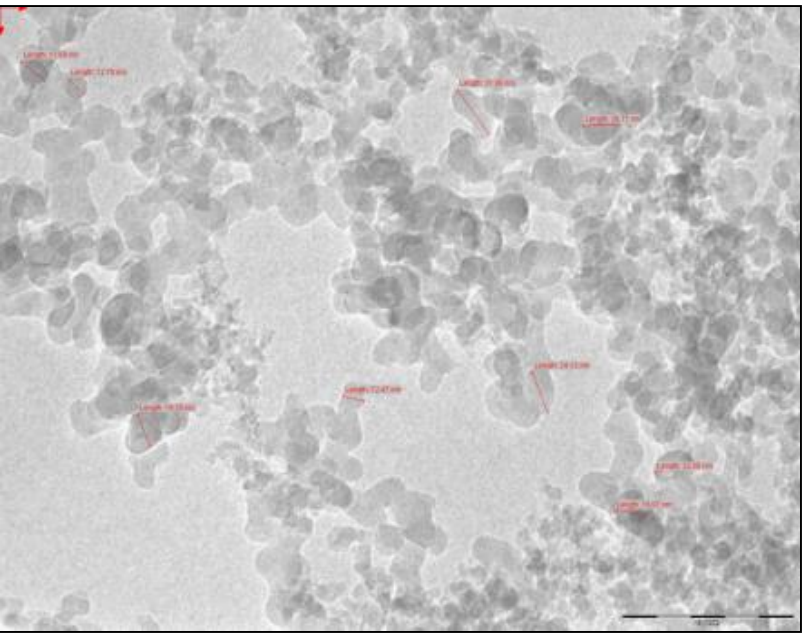


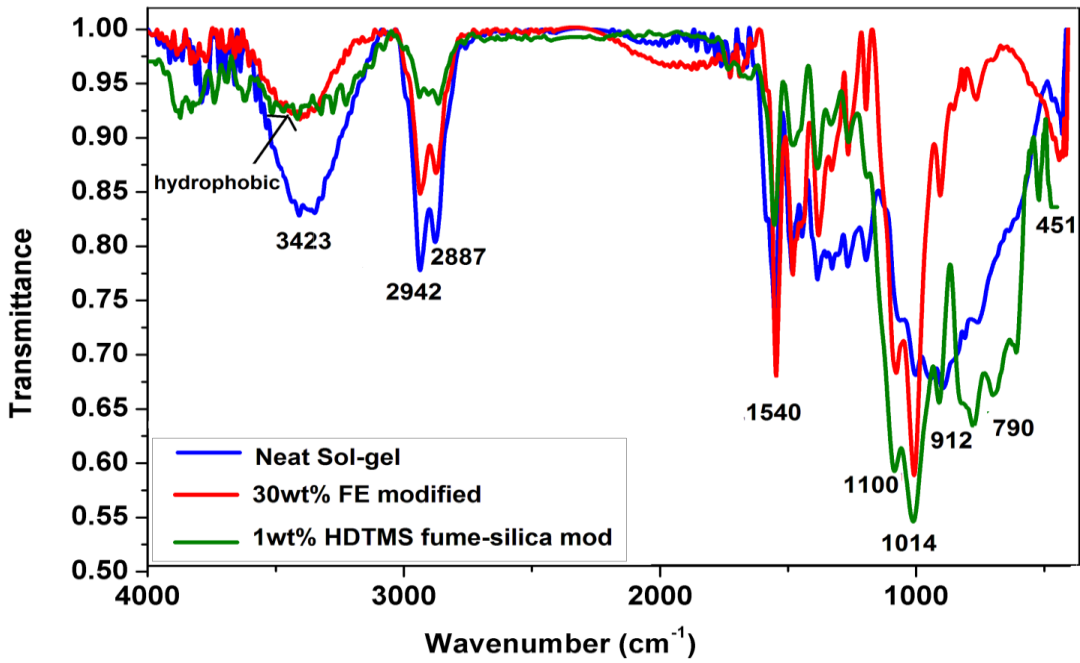




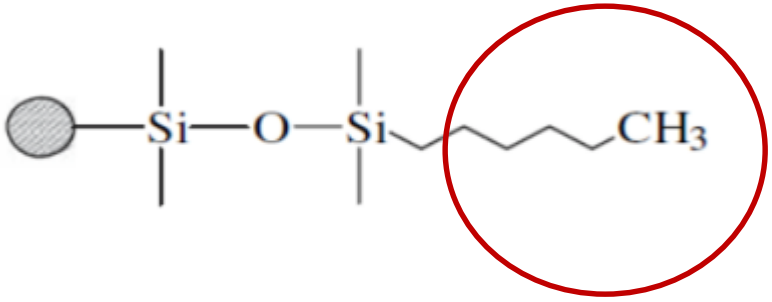
- Maximum contact angle achieved after nano-ZnO modification was 120°
- Nano-ZnO resulted in improved sliding angle of about 65°
- A shift from Wenzel state to Cassie Baxter state was observed

Modification of FE-sol with HDTMS silica nano-particle

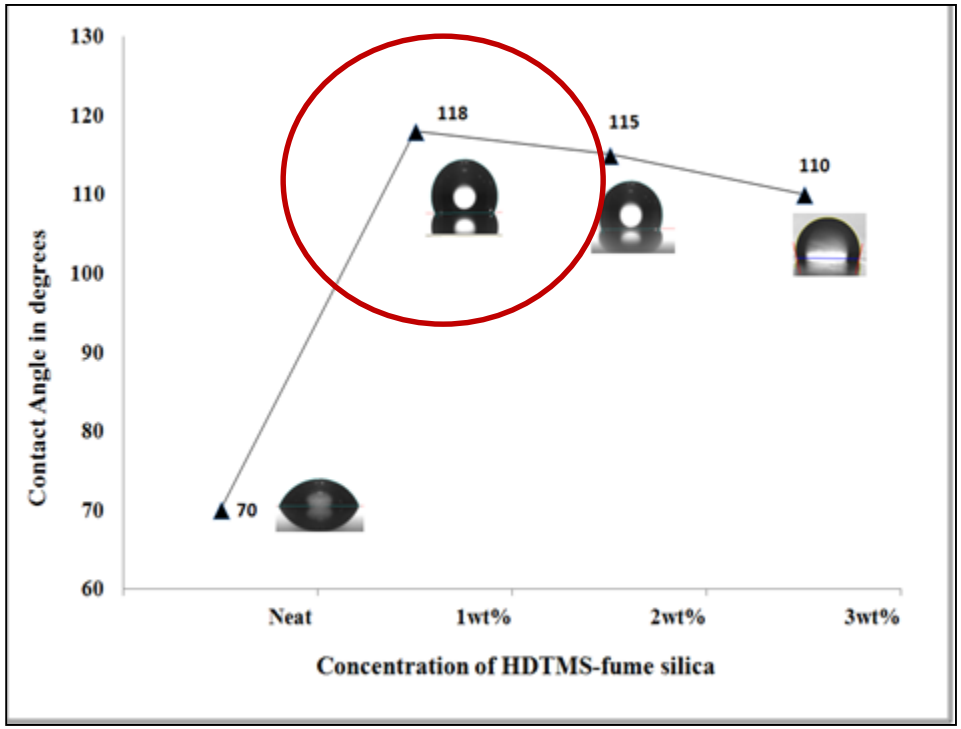


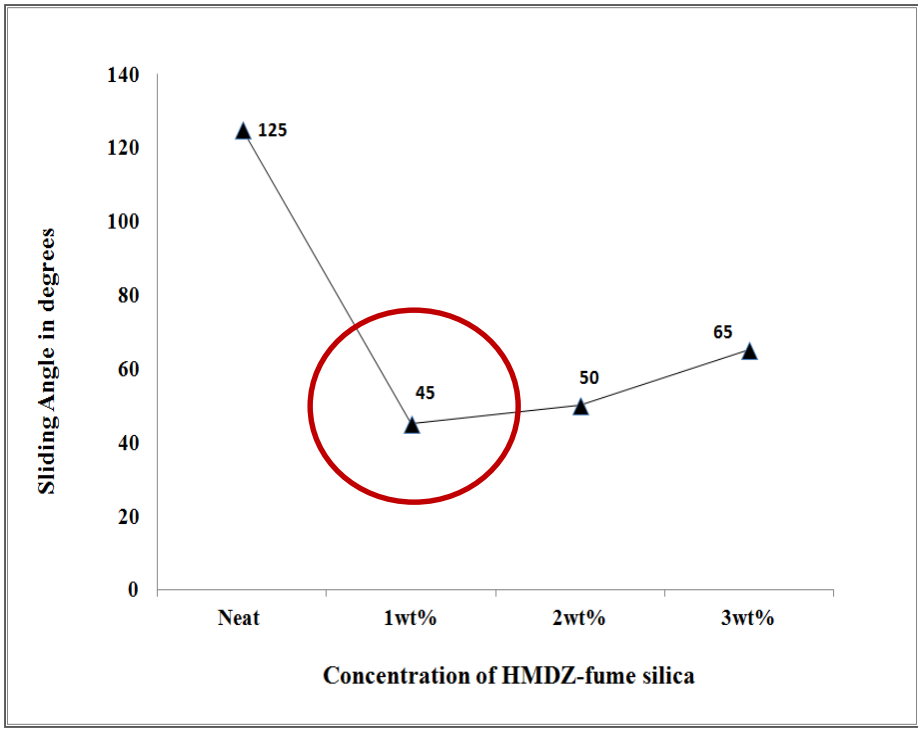


- Particle size – 15-25nm
- BET surface area - 85±20 m^2/g
- Hydrophobic modification with long chain C16 organo-silane
- Hence, HDTMS modification resulted in reduced surface energy due to long hydrophobic non-polar chains



Hexa -decyl trimethoxysilane nano-silica

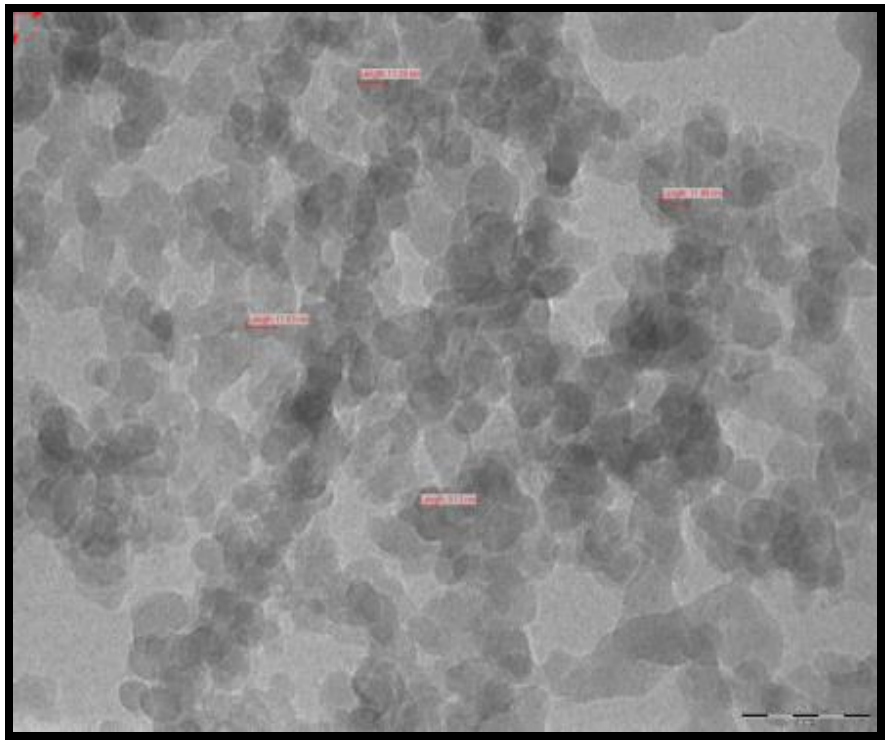


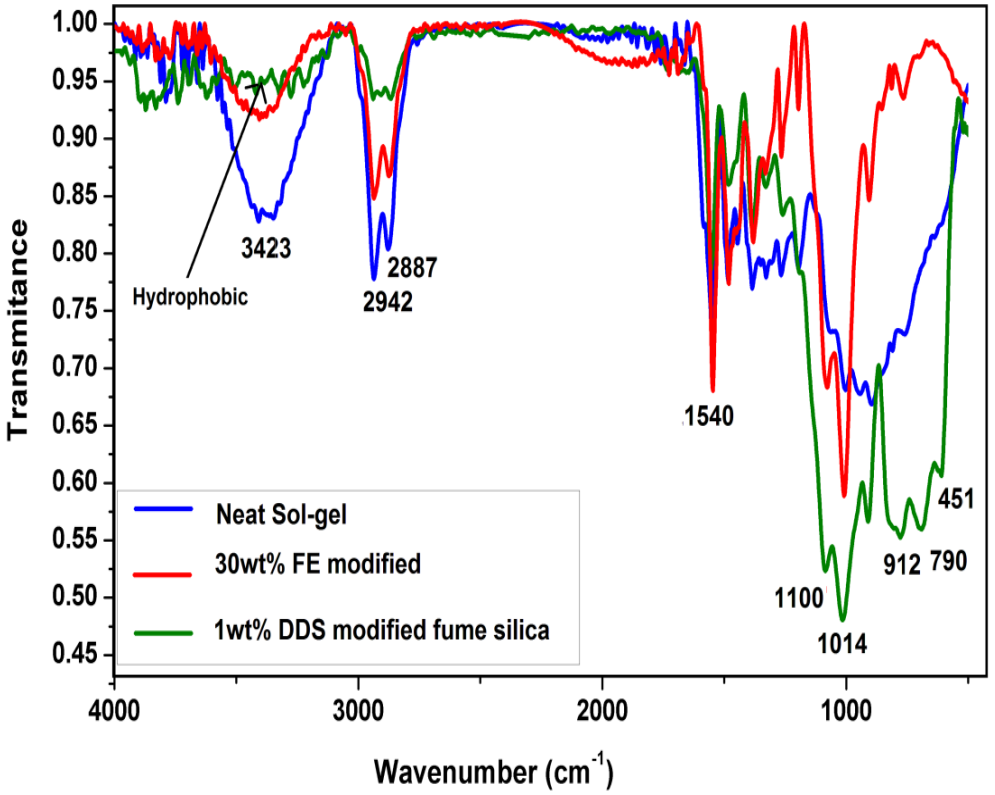


- Maximum contact angle achieved after HDTMS –nano silica modification was 118°
- Significant improvement in sliding property was observed , SA ~ 45°
- Hence, significant shift from Wenzel state to Cassie Baxter state



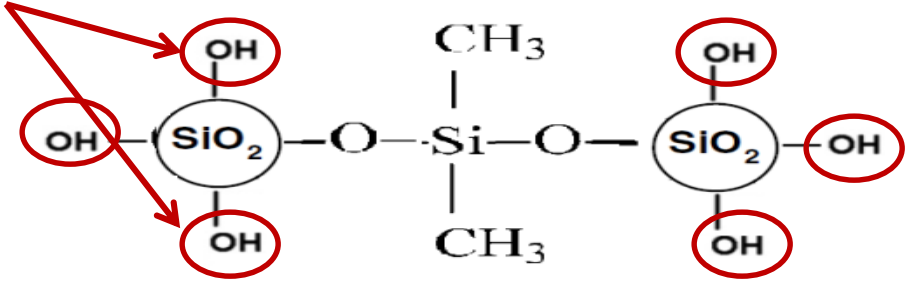
Modification of FE-sol by DDS nano-silica particles



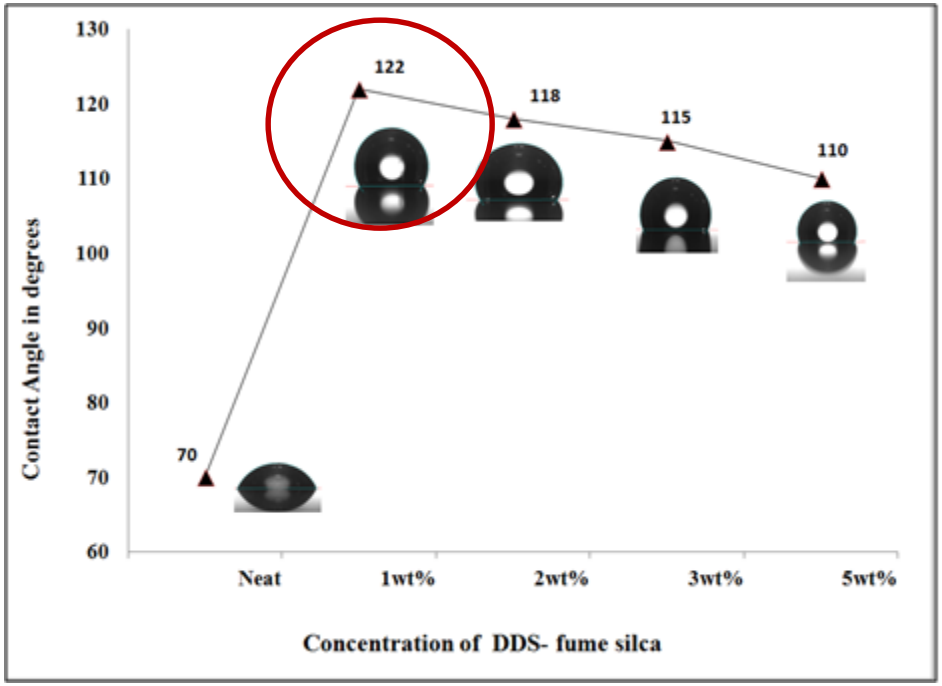


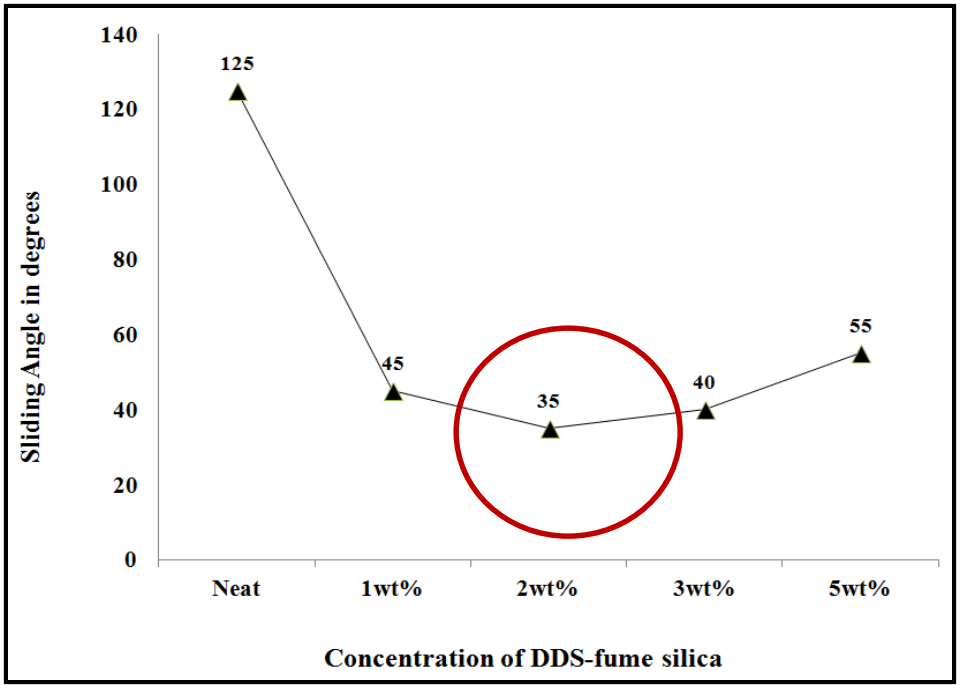
- Particle size – 10-15nm.
- BET surface area - 115±10 m^2/g.
- Hydrophobic modification with **di-methyl** group.
- Reduction in surface energy due to non-polar di-methyl groups.
- Better dispersion of nano-particles due to small size and large surface area.

Remaining –OH groups



Dichlorodimethylsilane modified nano-silica

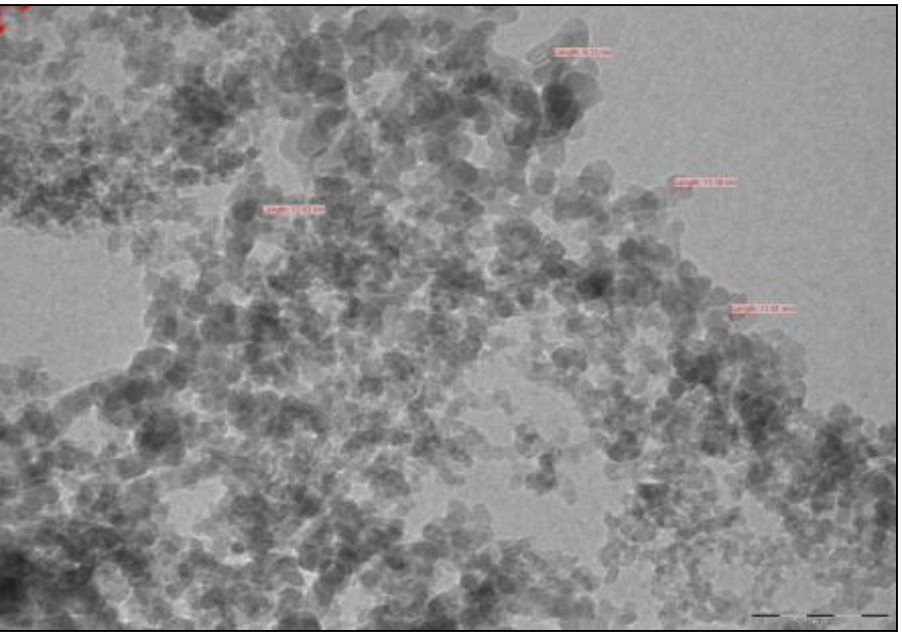


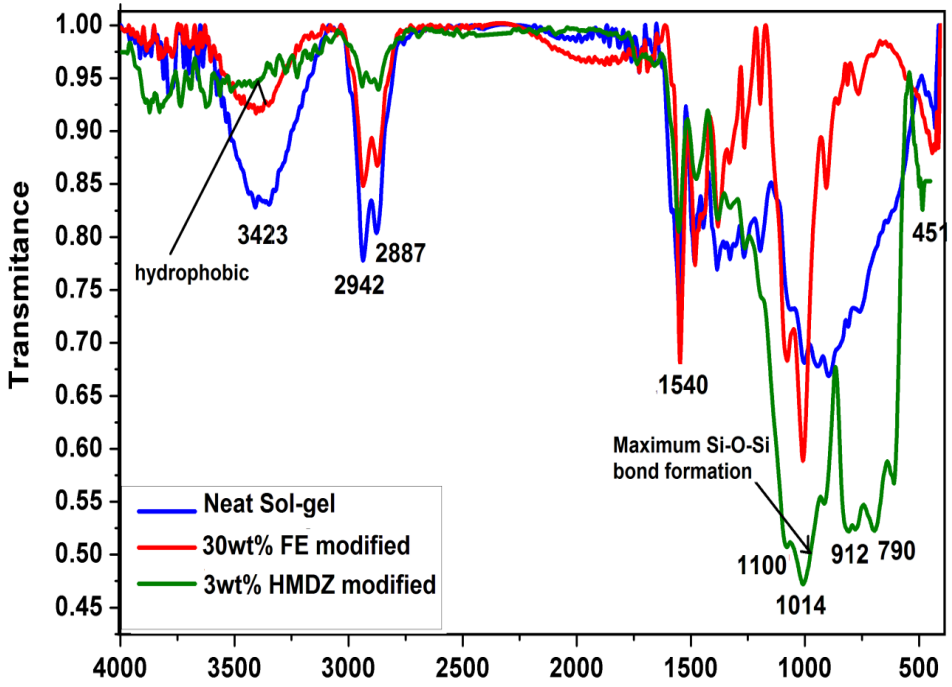


- Maximum contact angle achieved after DDS –nano silica modification was 122°
- Significant improvement in sliding property was observed , SA ~ 35°
- Hydrophobicity lay in Intermediate state

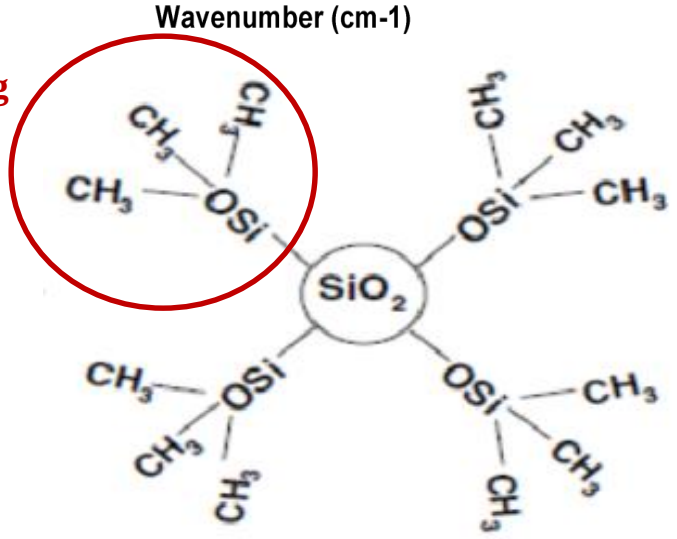


Modification of FE-sol with HMDZ nano-silica particles

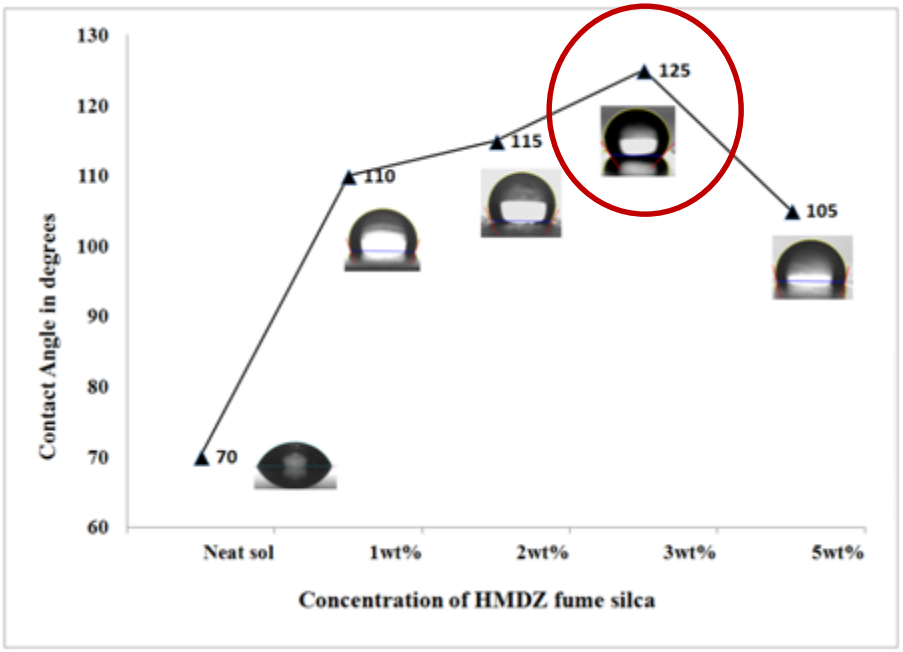


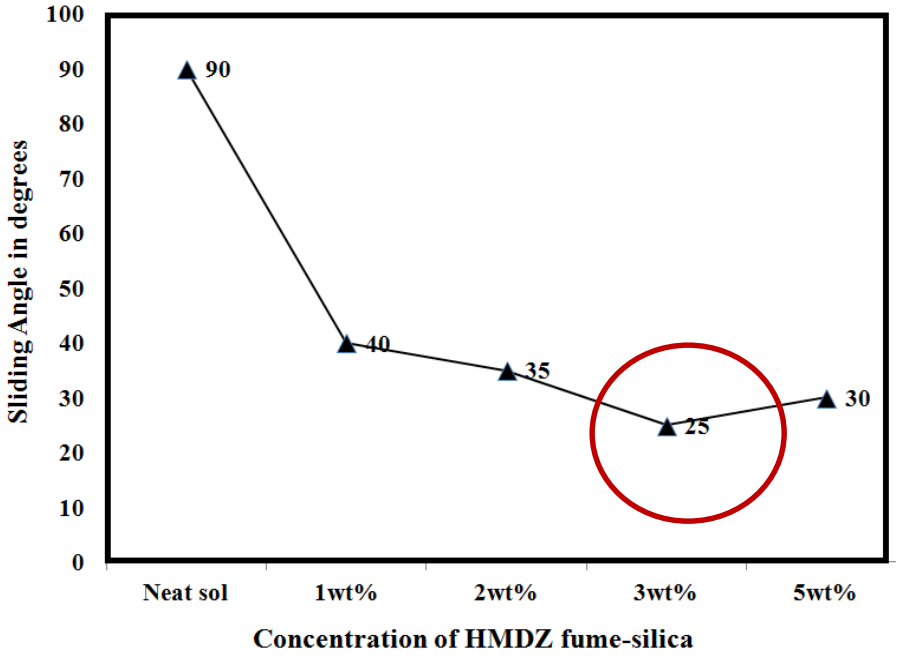


- Particle size – 7 -10 nm.
- BET surface area –160± 25 m^2/g.
- Hydrophobic modification with **tri-methyl** group.
- Reduction in surface energy due to non-polar tri-methyl groups.
- Very good dispersion of nano-particles due to smallest size and largest surface area amongst all.

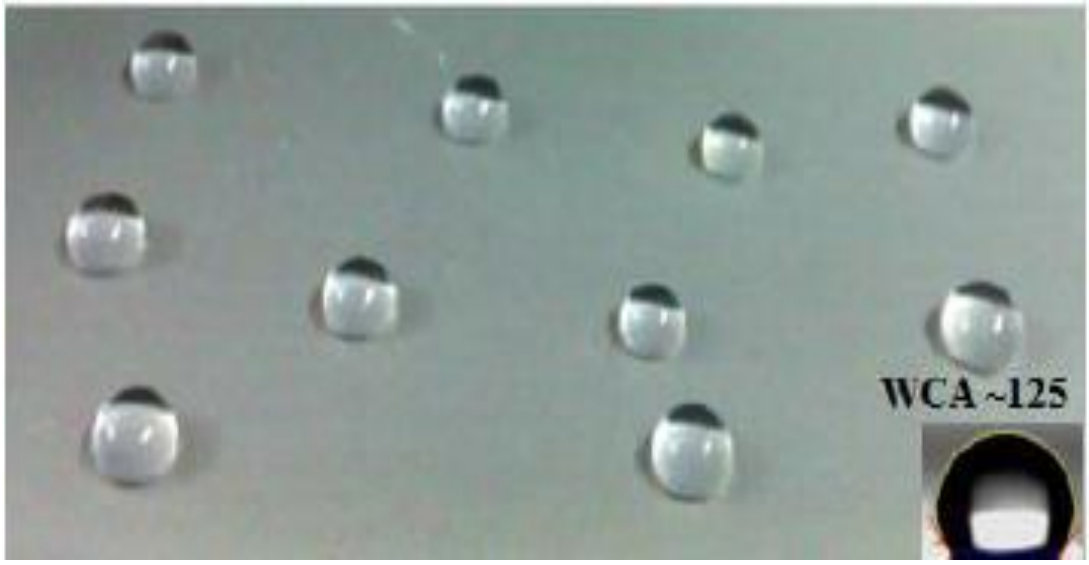


Hexamethyldisilazane nano-silica



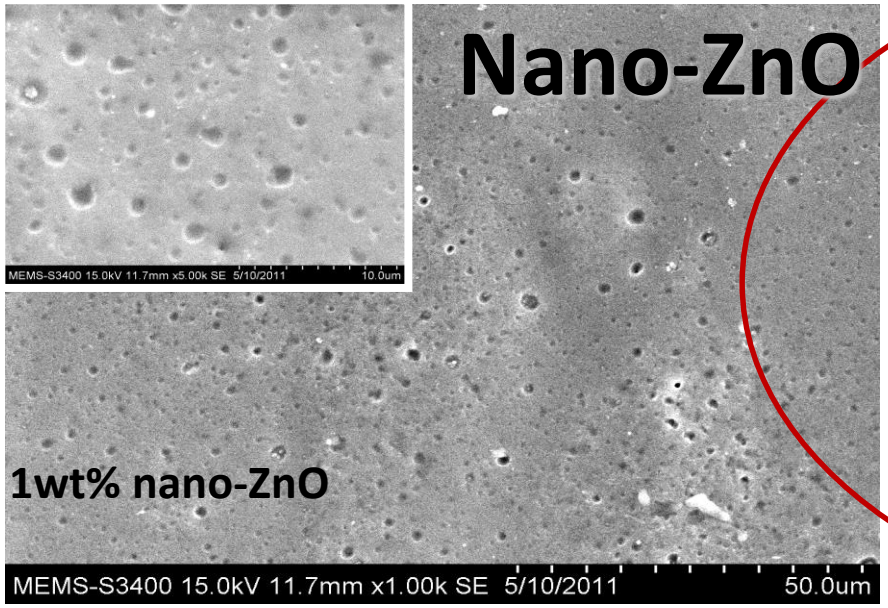


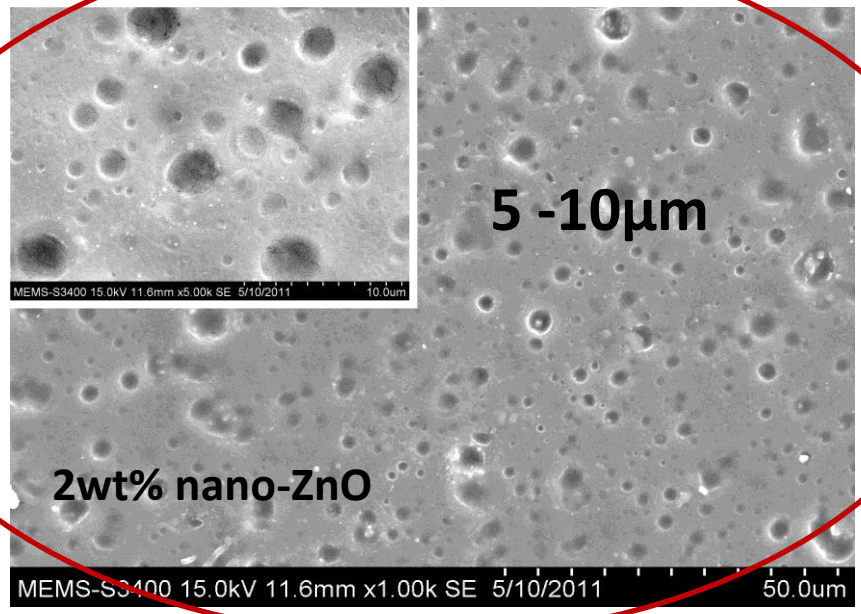
- Maximum contact angle achieved after HMDZ –nano silica modification was 125°
- Excellent sliding property was observed , **SA ~ 25°**
- Significant shift from Wenzel to Cassie Baxter state

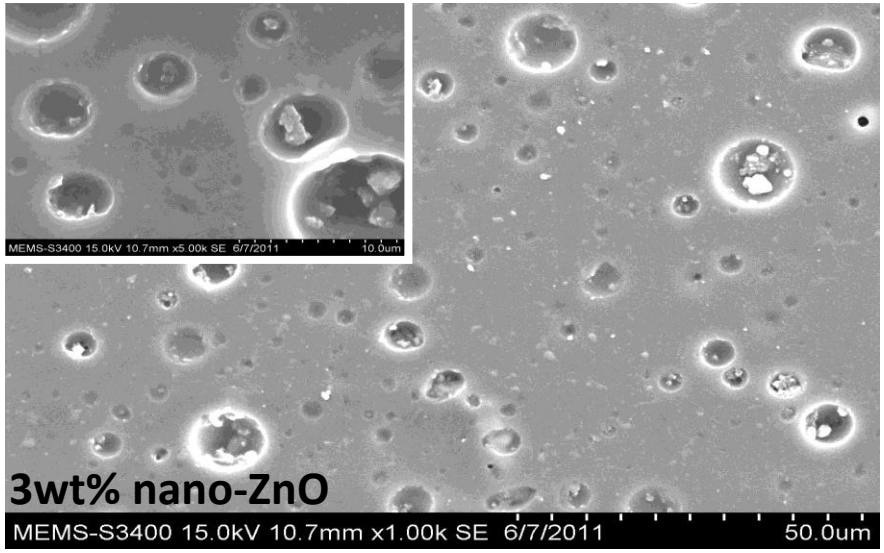


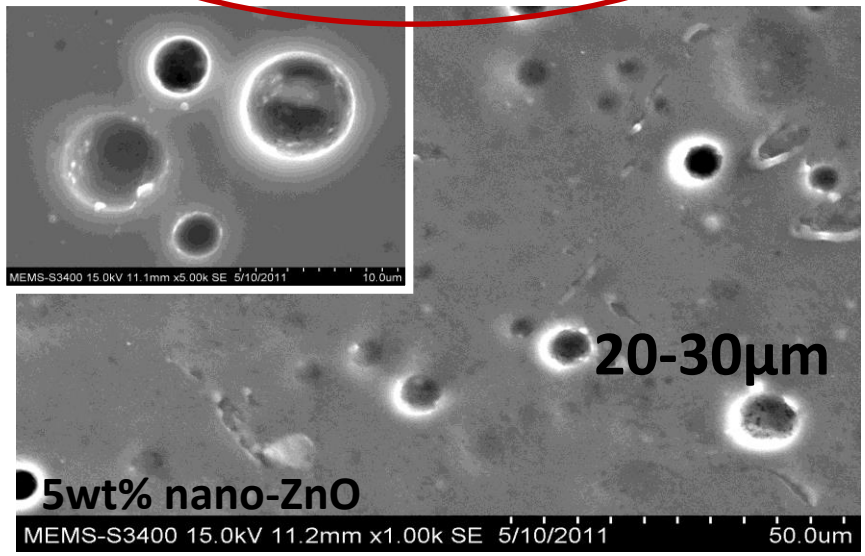
Comparison of various nano-particle incorporated sol-gel coatings

Nano-particle	Particle size (nm)	BET surface area ($g/m^{2)}$)	Average Contact Angle (º)	Average Sliding angle (º)
Nano-ZnO	30-40	45±20	120	65
HDTMS-nano-silica	15 -25	85±20	118	45
DDS nano-silica	10-15	115±10	122	35
HMDZ nano-silica	**7 to 10**	**160± 25**	**125**	**25**



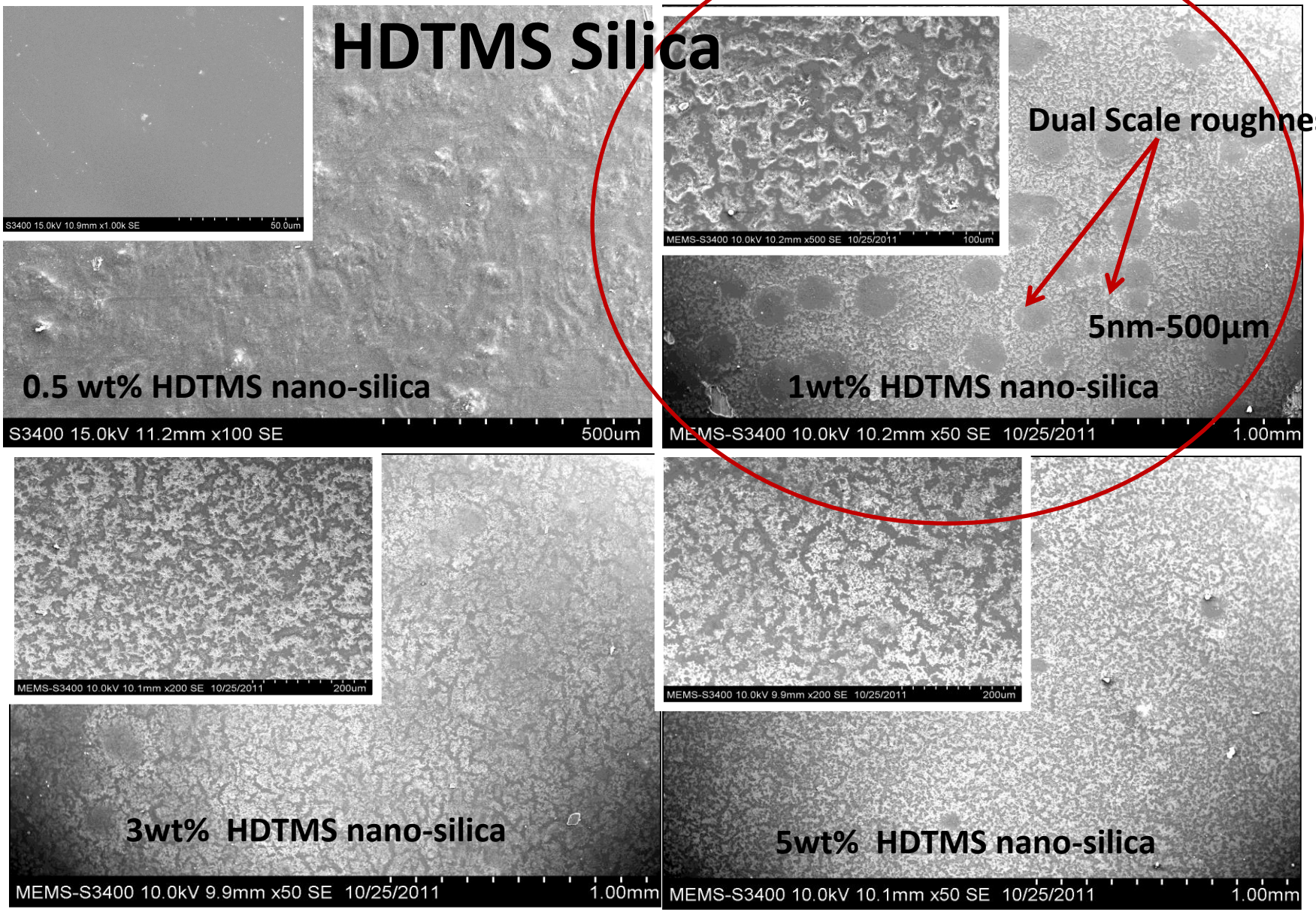






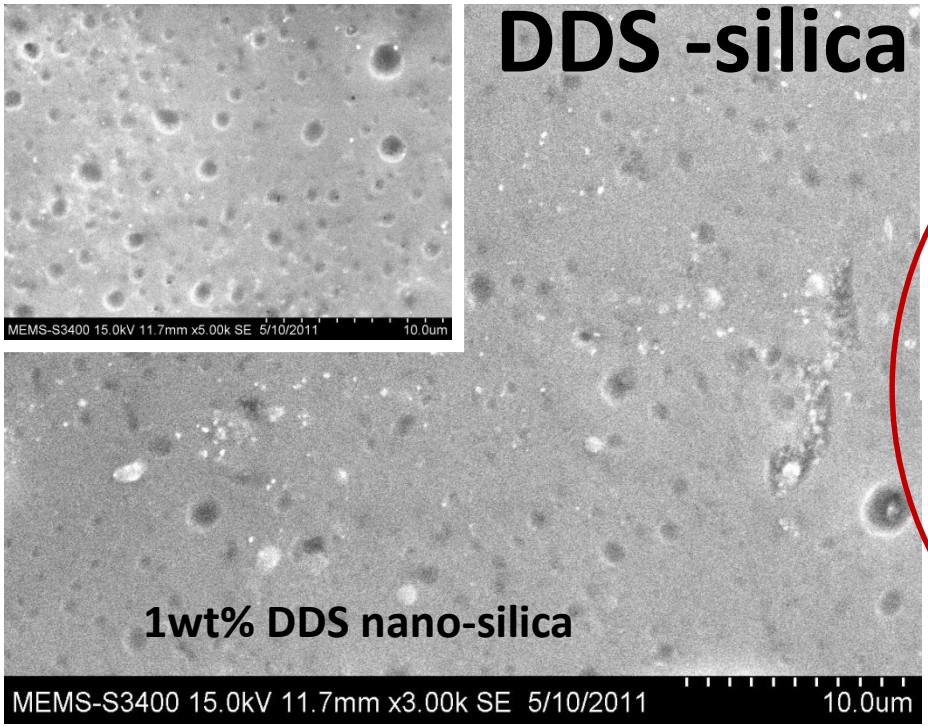
❑After nano-ZnO addition ,microspheres of diameter **5-10µm** were overlapped with **30µm** craters of FE-sol below ,hence creating a **dual scale roughness**

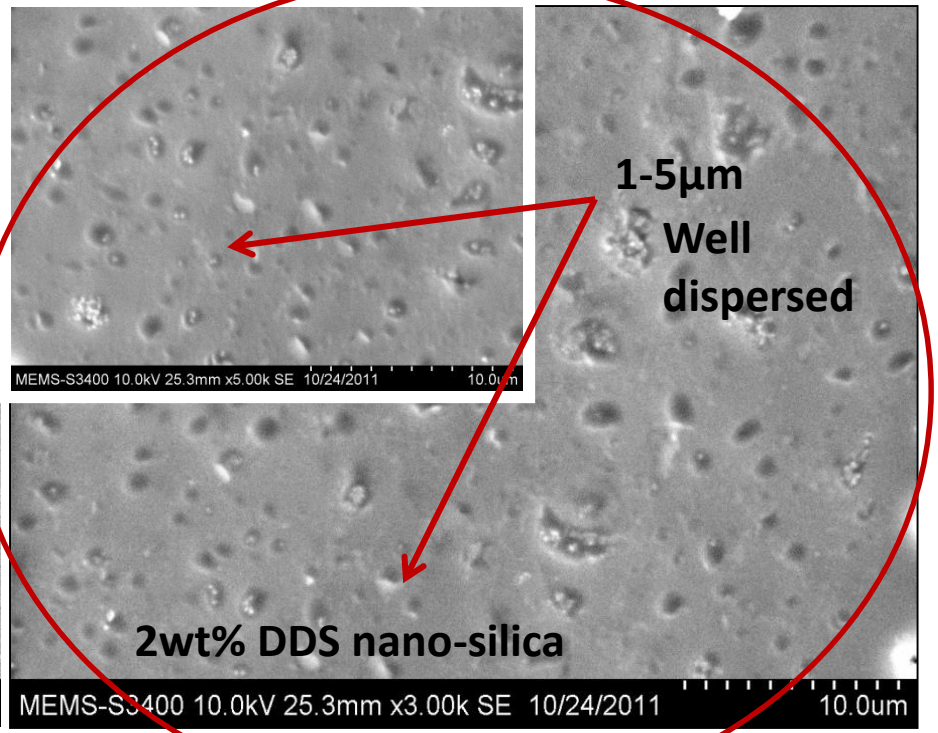
❑This dual scale roughness was responsible for improvement in hydrophobicity

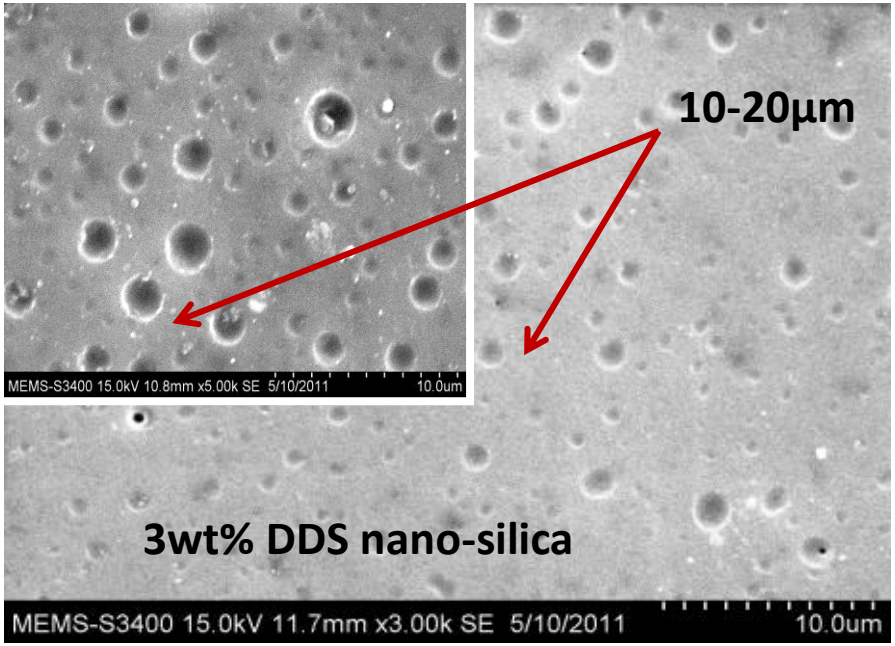


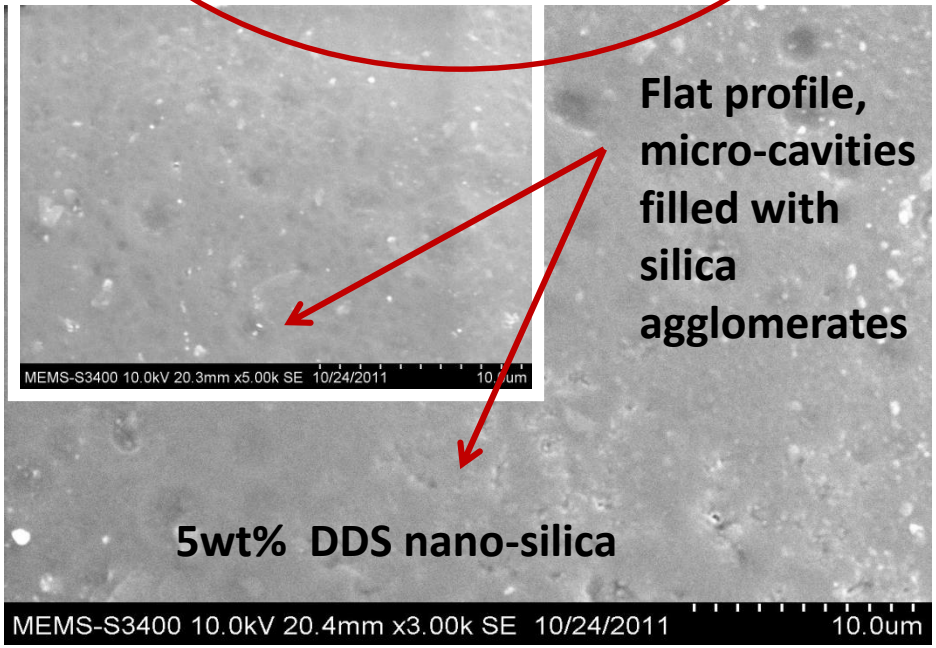
- Dual scale roughness ranging from several nm-500µm was achieved at 1wt%-: Sheet like structure
- Such roughness pattern resulted in entrapment of layer of air resulting in improved sliding behaviour
- At higher concentration s extensive agglomeration resulted in wax like viscous sol-gel : Difficult to apply

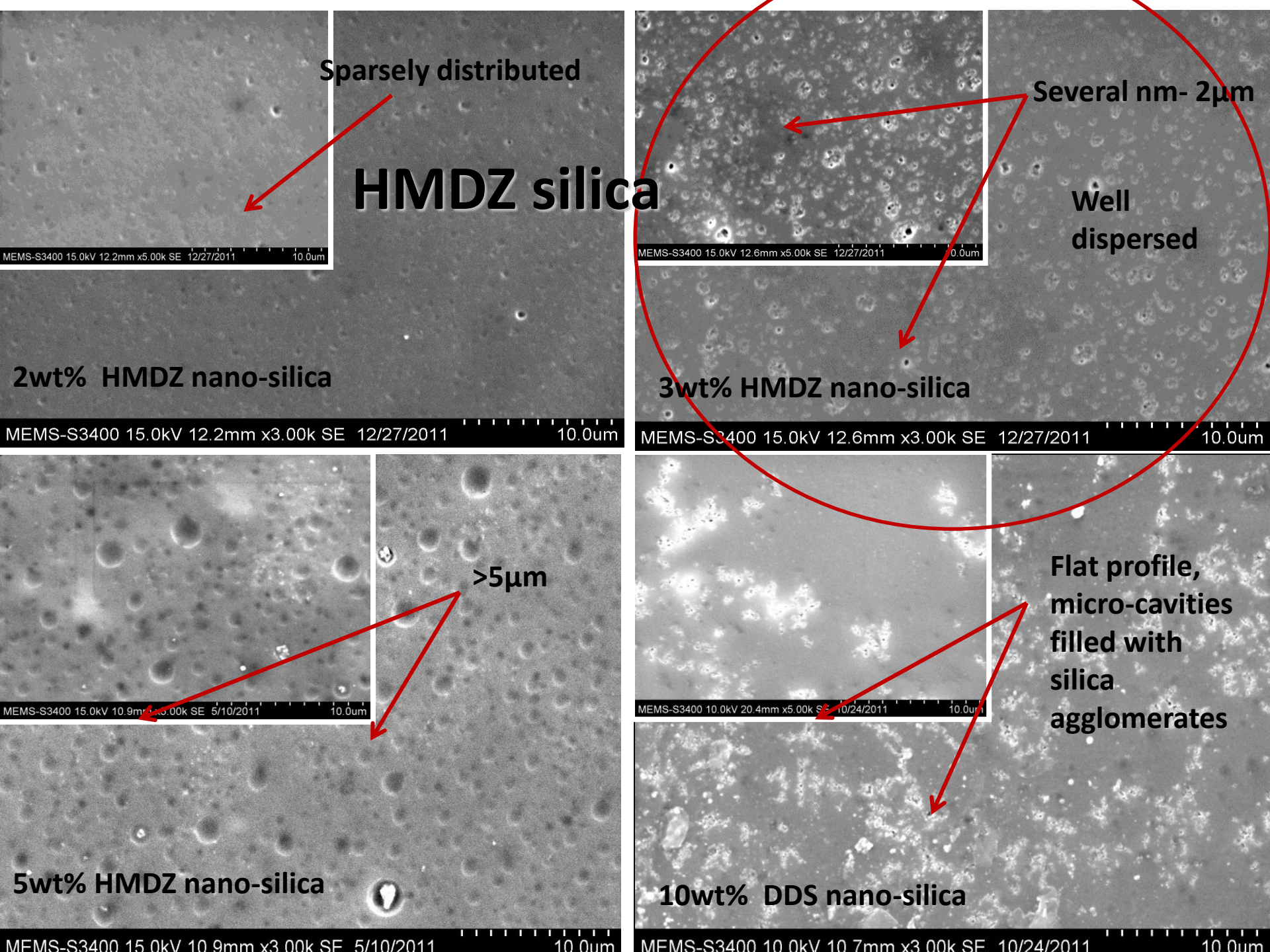
DDS -silica

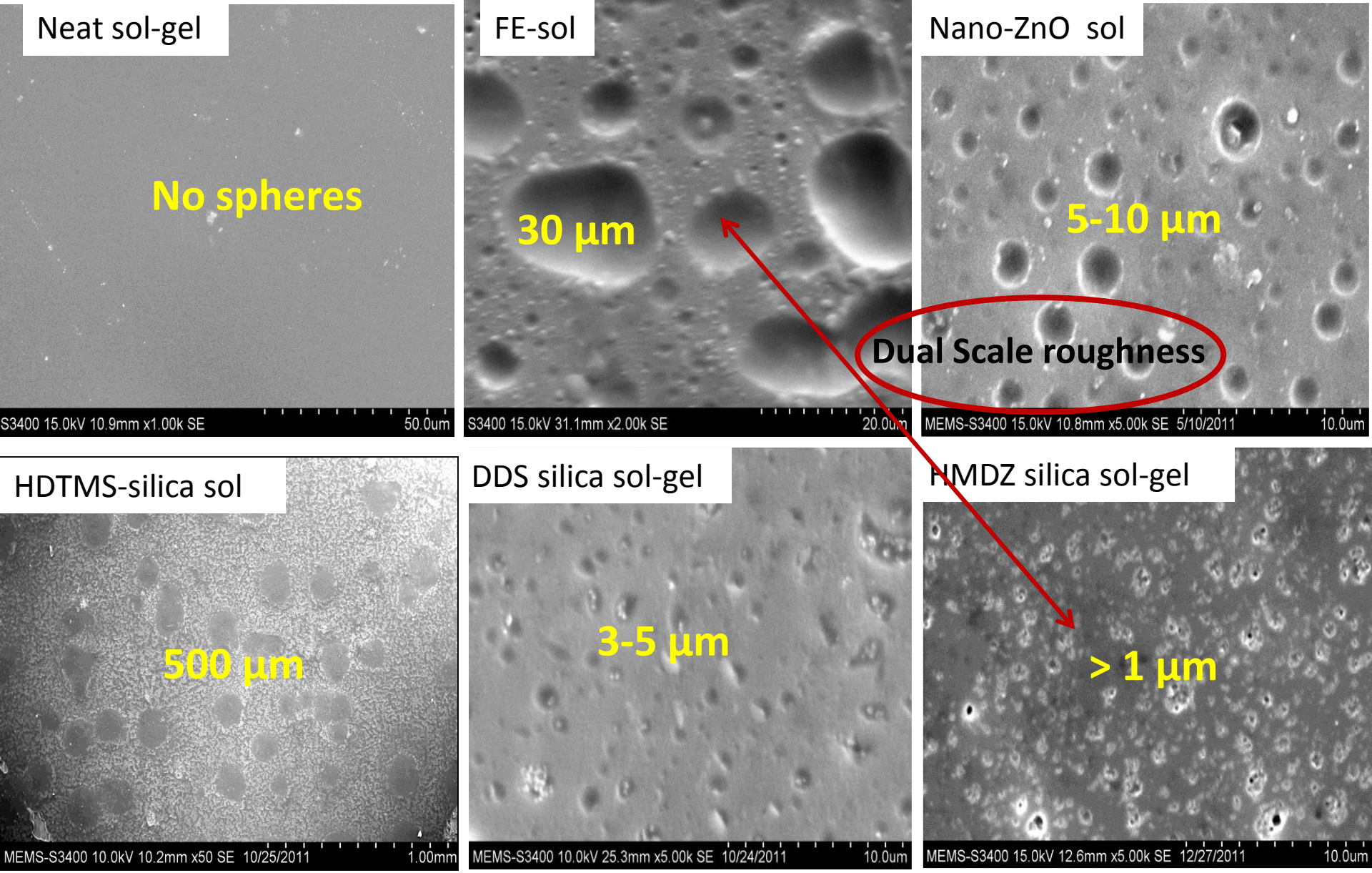

1wt% DDS nano-silica
MEMS-S3400 15.0kV 11.7mm x3.00k SE 5/10/2011 10.0um


1-5µm
Well
dispersed
2wt% DDS nano-silica
MEMS-S3400 10.0kV 25.3mm x3.00k SE 10/24/2011 10.0um


10-20µm
3wt% DDS nano-silica
MEMS-S3400 15.0kV 11.7mm x3.00k SE 5/10/2011 10.0um


Flat profile,
micro-cavities
filled with
silica
agglomerates
5wt% DDS nano-silica
MEMS-S3400 10.0kV 20.4mm x3.00k SE 10/24/2011 10.0um

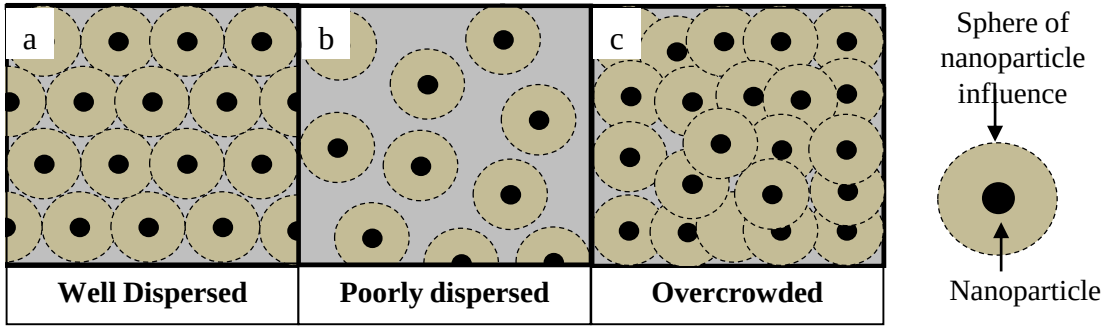

Sparsely distributed
HMDZ silica
Several nm- 2µm
Well dispersed
2wt% HMDZ nano-silica
3wt% HMDZ nano-silica
>5µm
Flat profile, micro-cavities filled with silica agglomerates
5wt% HMDZ nano-silica
10wt% DDS nano-silica



Micro-nano dual scale roughness is responsible for excellent sliding behaviour after nano-particle addition due larger fraction of air entrapment within the dual scale roughness pattern

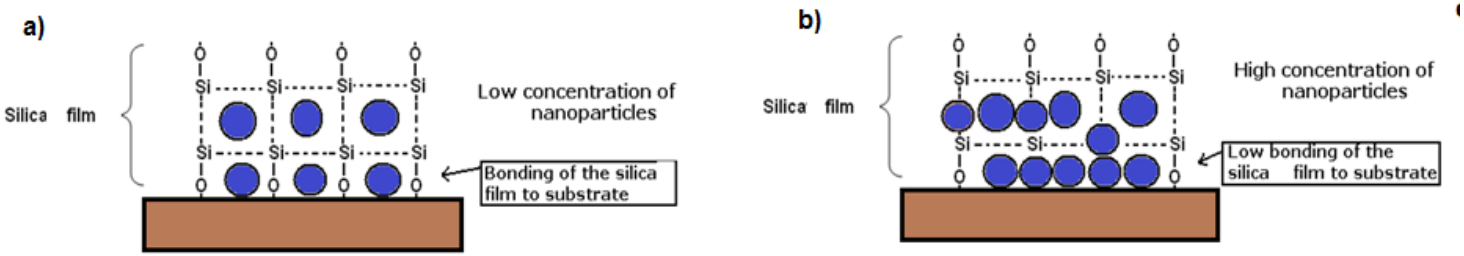
Theories of nano-particle distribution

❑ As per **the *Continuum Theory***, which means that the effect of each nano-particle distributed in coating matrix has its range of influence. In case nano-particle is overcrowded or non-uniformly distributed, the range of influence gets disturbed and the optimum property is lost



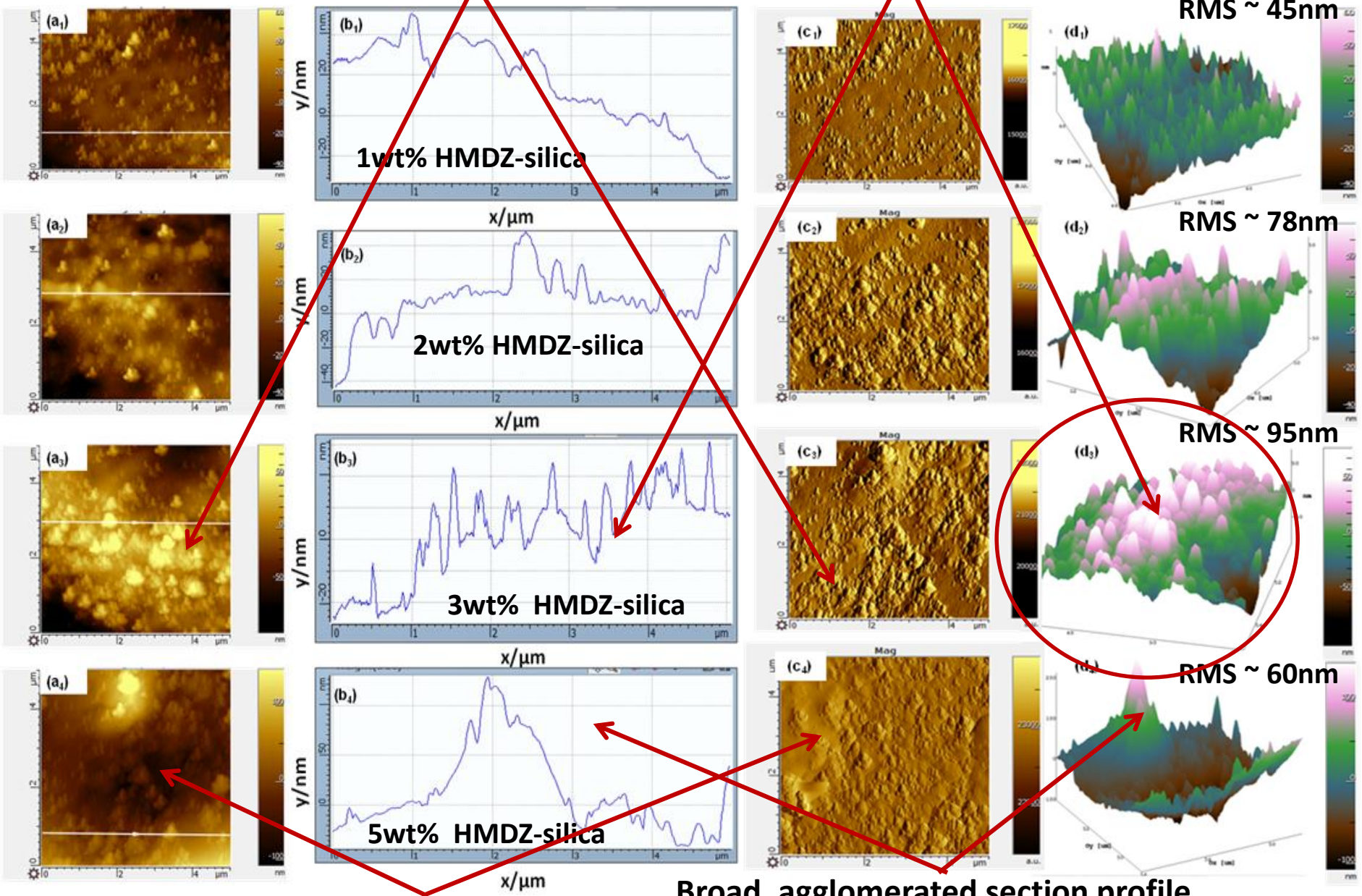
❑ At low concentration nano-particles tend to distribute uniformly without effecting the Si-O-Si bond formation during curing as well as Si-O-M bond required for adhesion with substrate.

❑At higher concentrations large agglomerates leads to low bonding of sol-gel network to the substrate thereby resulting in poor mechanical properties.



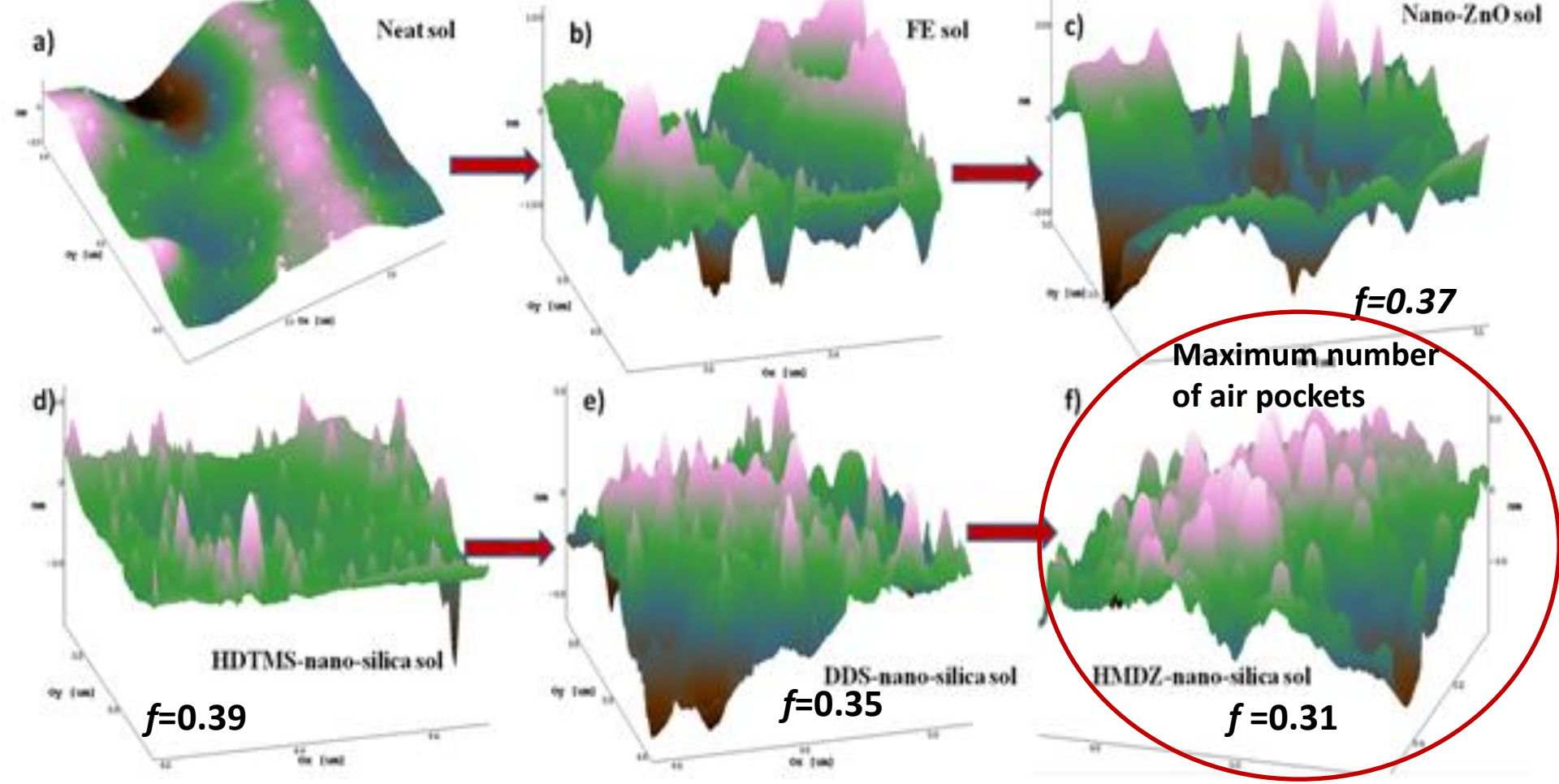
Uniform distribution of nano-particles@ 3wt%

Number of peaks with “Max height” increases



Highly agglomerated

Broad, agglomerated section profile
Responsible for spreading of water



❑ **Area fraction of solid surface (*f*)** can be calculated from Cassie- Baxter equation

$\cos\theta r = f(\cos\theta s + 1) - 1$,

θ_r (120°, 118°, 122° and 125°) and θs (70°) are contact angles of rough and smooth surface

❑ Low value of ***f*** for HMDZ implies that modification resulted in exposure of water droplets to comparatively **larger portion of air** and offers high resistance to wettability which supports high values of contact angle and sliding angle

Sliding ability of the coatings

One of the limitation of the formulations made for enhancing hydrophobicity such as fluro addition or fluro + nano-ZnO, the sliding angle was not good (Wenzel Stage) – where, though we get hydrophobic effect however the beed is struck betwwen roughness groves, hence does not slide.

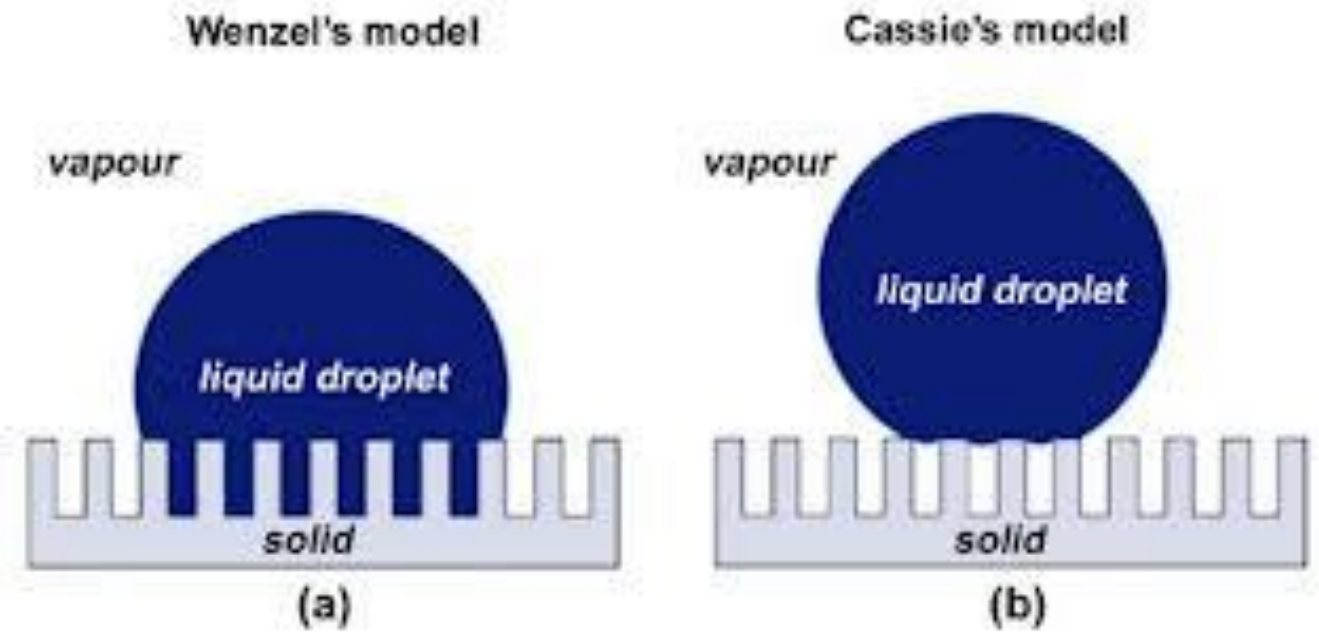
So in order to improve the sliding angle, the nano particles added must be modified hydrophobically by using various silane precursor, such as HMDZ (hexamethyl disilazane, DDS – dimethyl dichlro Silane etc.) – Cassie State

Though we modified ZnO by oelic acid and TEOS, but results were not effective.

Mechanism of Hydrophobicity

$Cos\Theta_w = Y\ Cos\ \Theta_v$

$Cos\Theta_{cb} = Y_f\ f\ Cos\ \Theta_v + f - 1$



Once the surface is in Cassie State, its sliding angle is also good and helps in Lower sliding angle and aids for Self Cleaning

❑ **Work of adhesion (W)** estimates the ease with which water drops moves on the surface

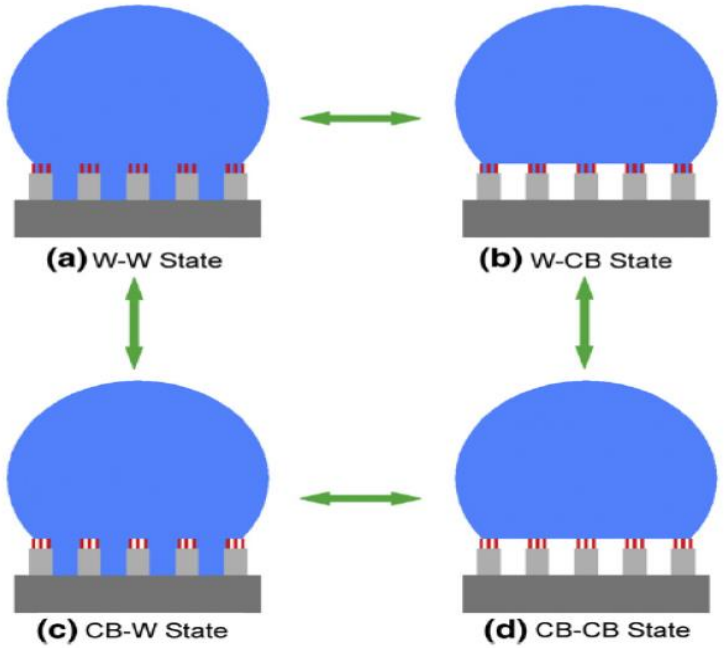
$$W=\gamma_{LA}f(1+\cos\theta)$$

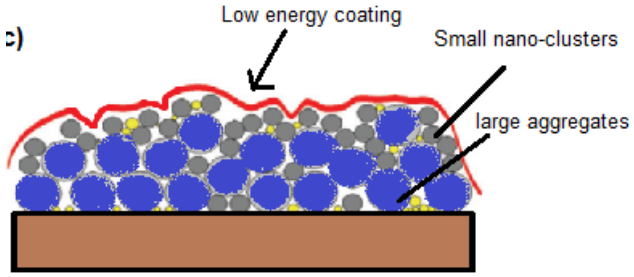
❑**Neat Sol (w) = 97.95mN/m** and **HMDZ-FE sol (W) 11.31mN/m.**

❑The decline of W from 97.95mN/m for neat sol-gel to 11.31mN/m for HMDZ-FE composite sol-gel coating indicates that the water droplets are partially suspended on a layer of air decreasing the interaction between the solid and liquid phases.

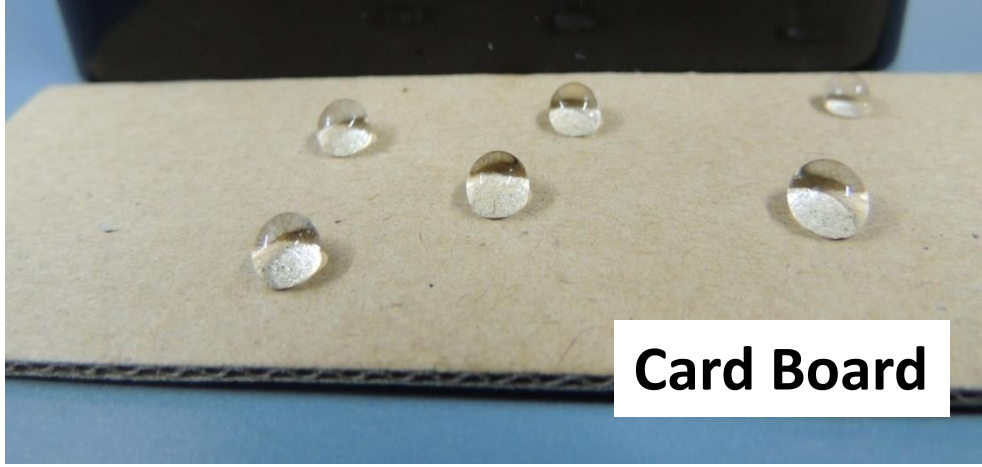
❑ Furthermore, **mixed state** can better explain the results because the contact angle of 125˚ achieved cannot be rationalized by the Cassie-Baxter scenario and small sliding angle of 15˚ which cannot be explained by Wenzel scenario

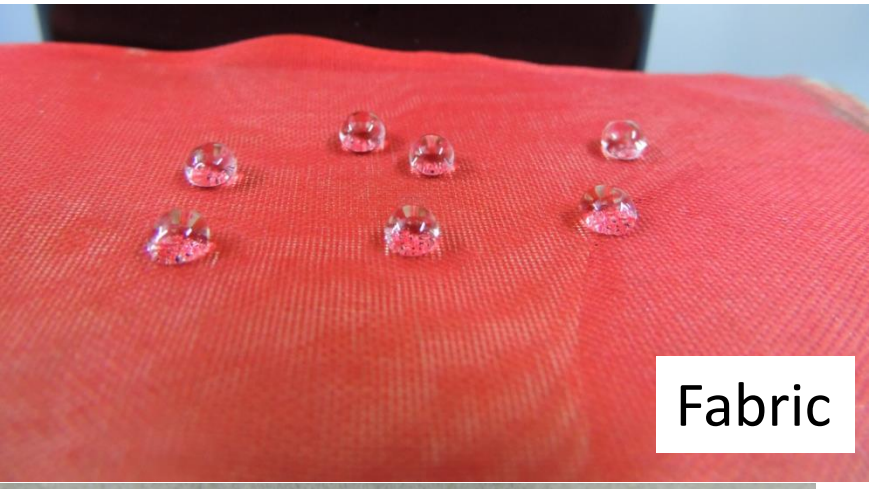
❑Hence both, **surface roughness** (93nm) due to HMDZ silica particles and **low energy** of perfluoro groups which migrate towards the surface were responsible for enhanced hydrophobic properties.

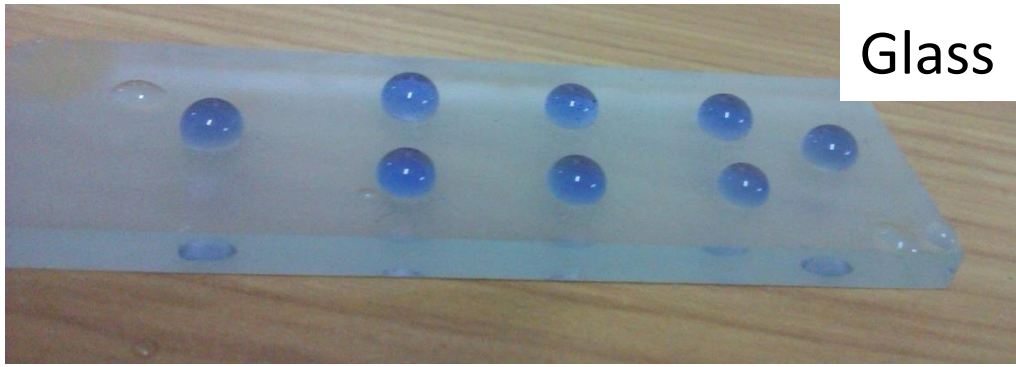


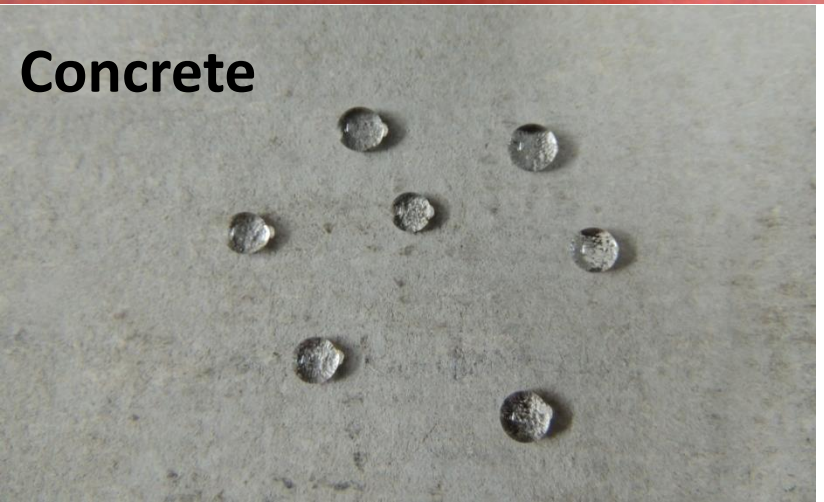



wood


Card Board


Fabric

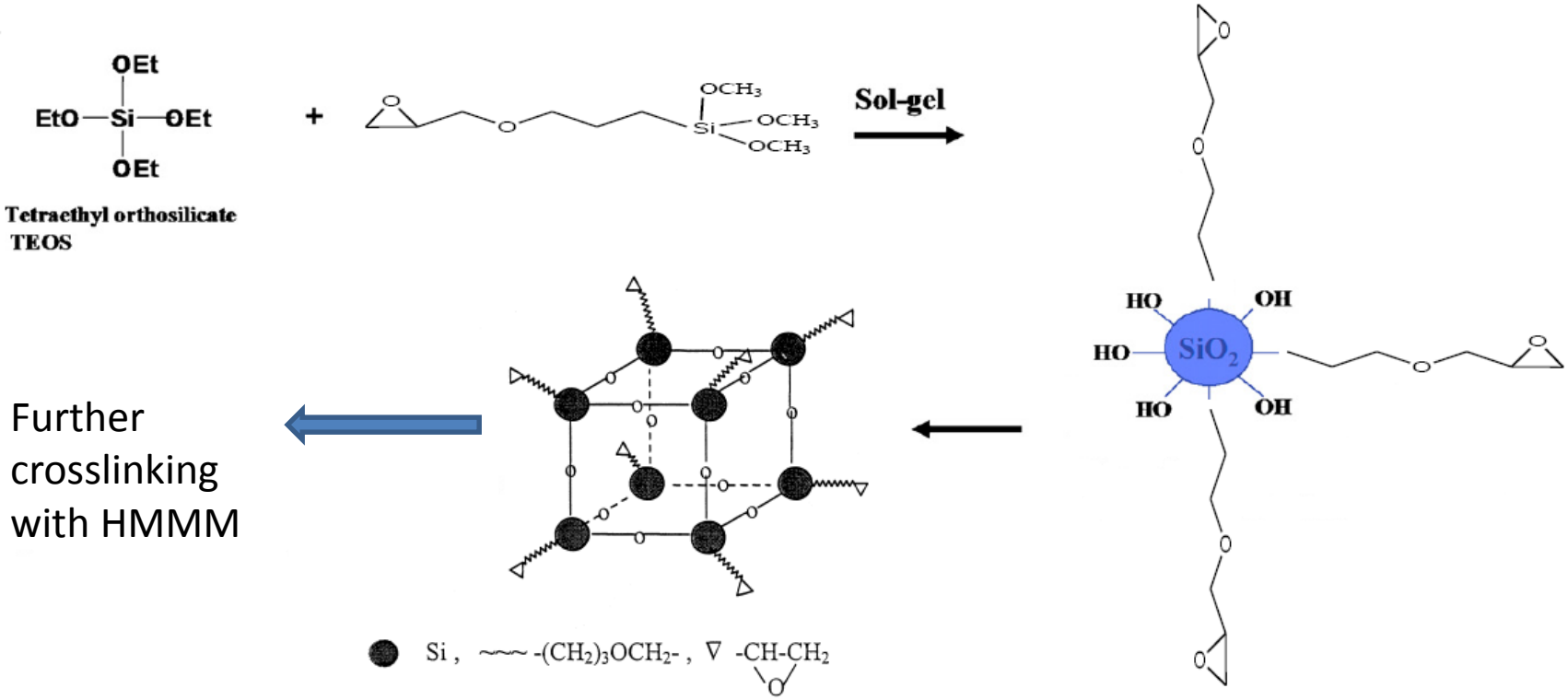

Glass

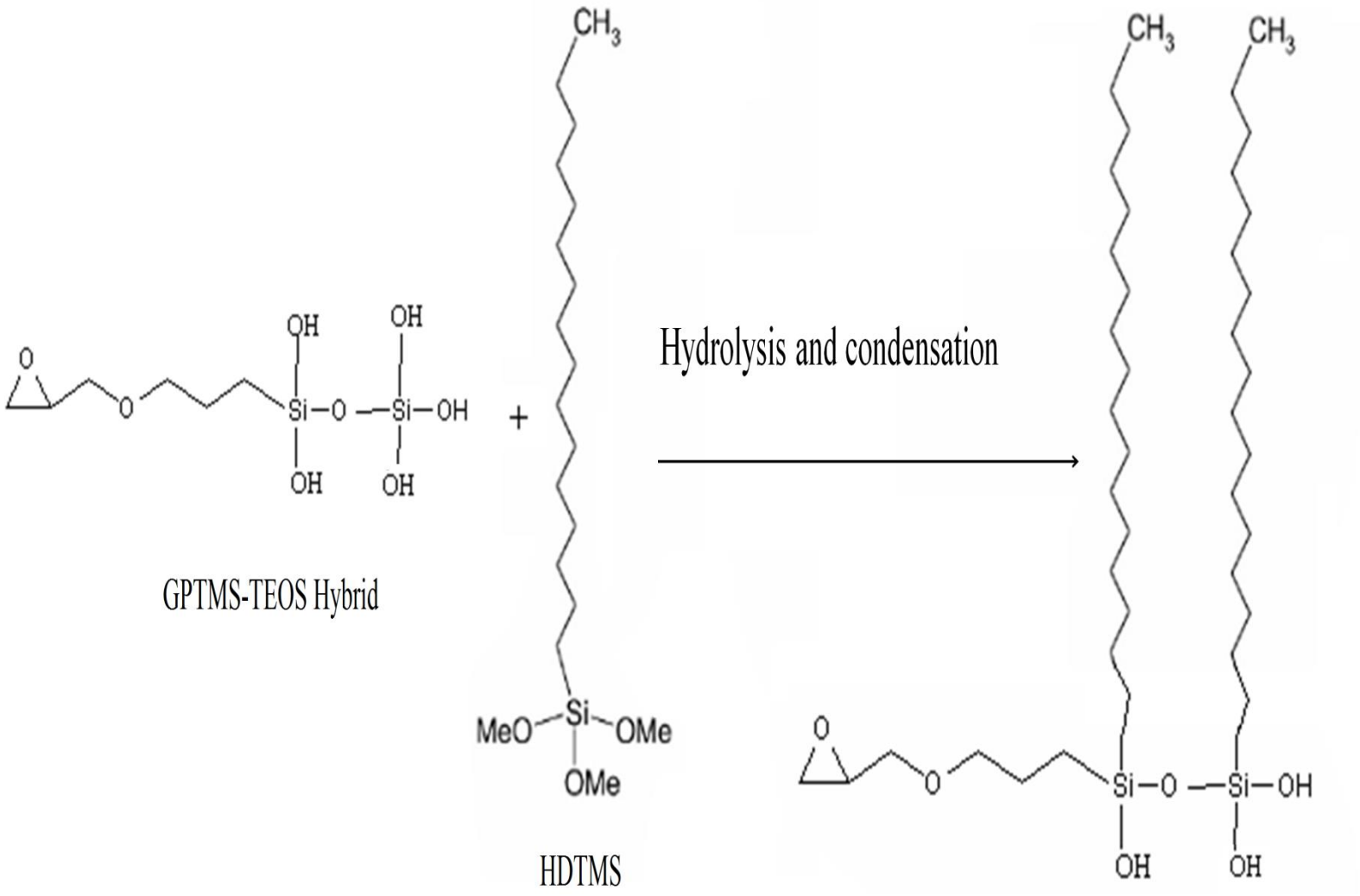

Concrete


Paper

Non Fluro Approach

Proposed mechanism of GPTMS and TEOS polymerization and condensation reaction.




Hydrolysis and condensation
GPTMS-TEOS Hybrid
HDTMS
GPTMS-HDTMS-TEOS hybrid sol-gel

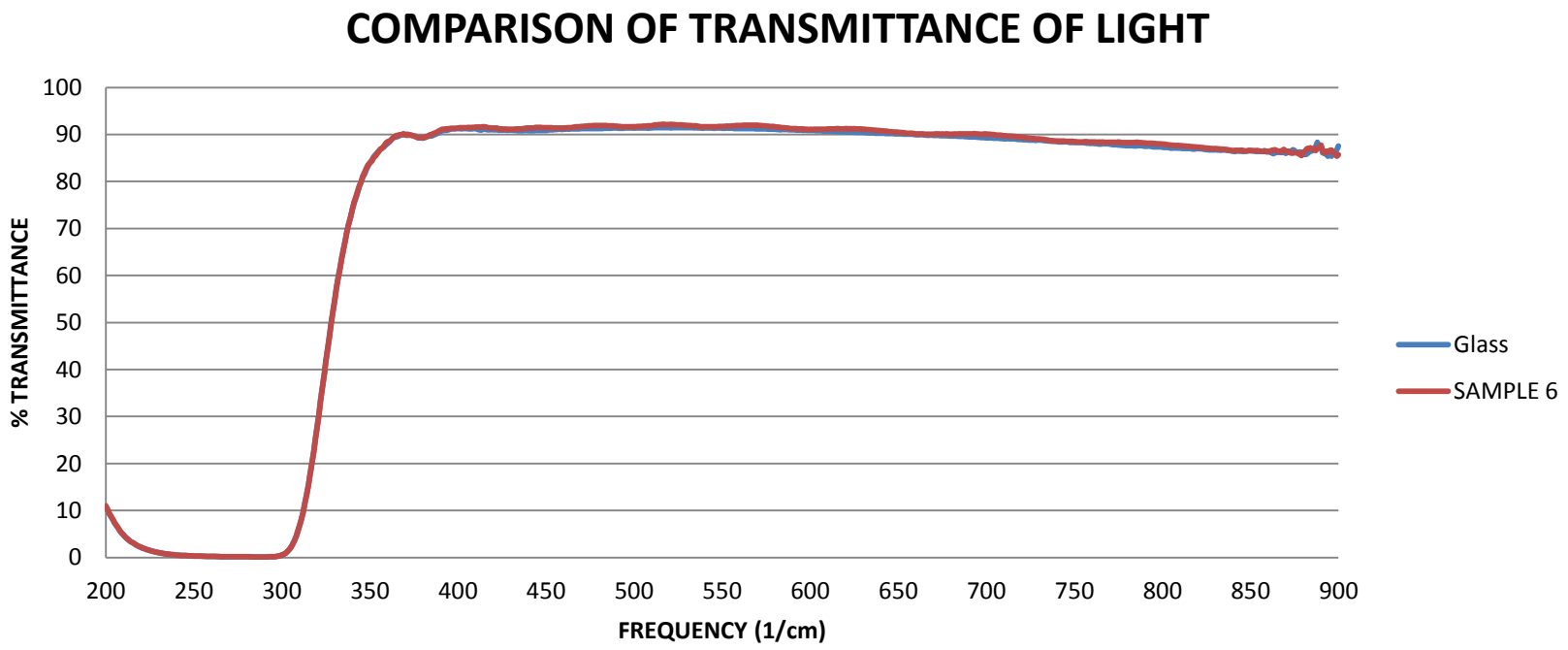
Composition of Various Sols Tried

Sample Designation	GPTMS	HDTMS	TEOS
A	0.5	1.5	8
B	2	2	6
C	1	3	6
D	1	3	8
E	1	3	12

Hexadecyltrimethoxysilane

PERFORMANCE OF COATING

- Coating has complete transmittance; same as glass
- Tested by UV-Visible Spectroscopy



- Coating has good adherence and life
- Contact angle of 109°

Applications



Glass on Buildings



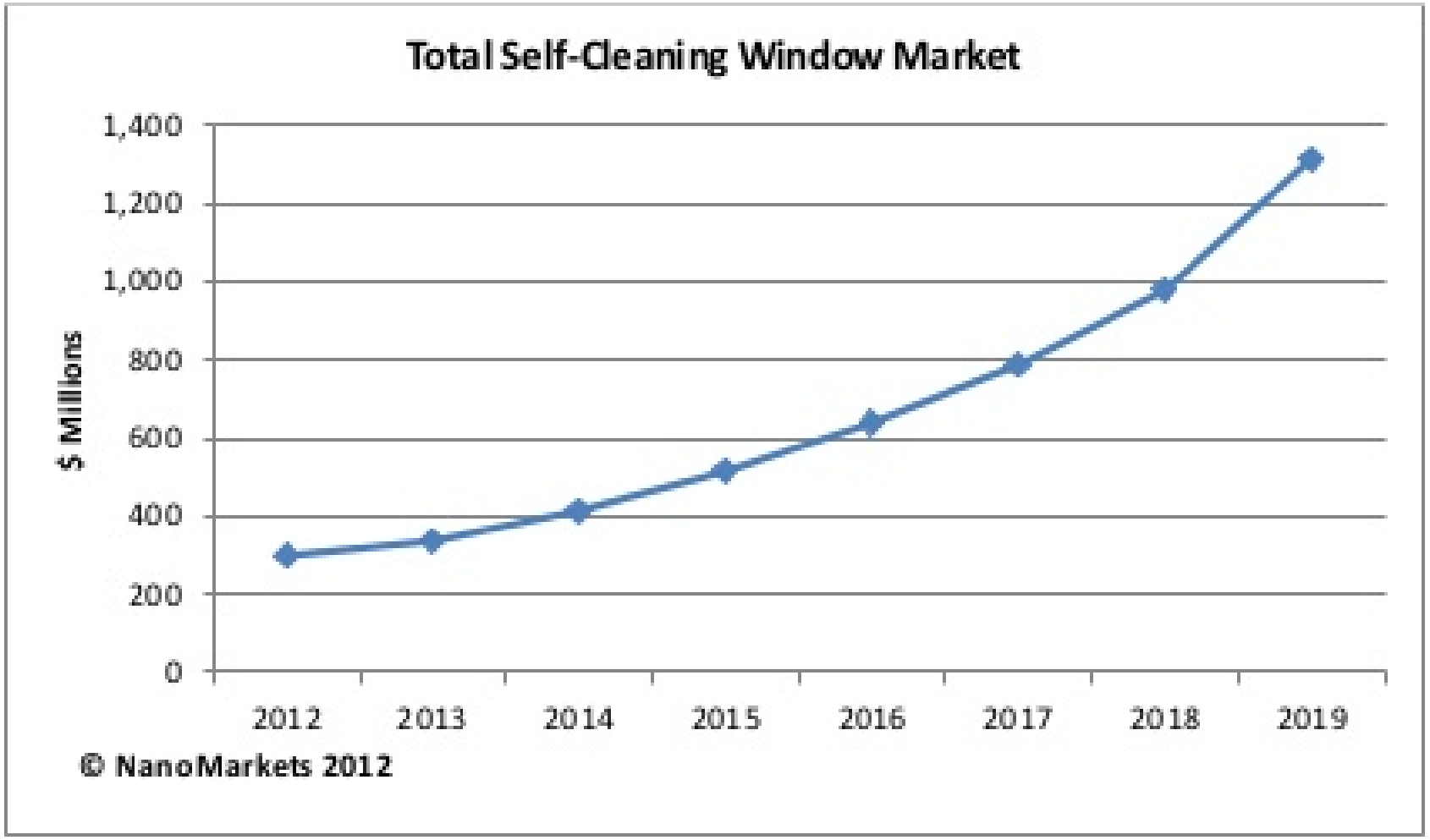
Solar Panels







furniture


Total Self-Cleaning Window Market
$ Millions
1,400
1,200
1,000
800
600
400
200
0
2012
2013
2014
2015
2016
2017
2018
2019
© NanoMarkets 2012

Where we stand today and what we have to do move forward?

- Industrialization of such products and their acceptability by users.
- Manufacturing in big volumes.
- Durability of the functionality – it is one of the biggest concrn.
- Cost

Acknowledgements

- **Ruchi Grover- Ph.D**
- Karan Thanewala
- Manish Bhadhu
- Vijay Kharod
- **K.Rajesh- Ph.d**