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Facultatea de Inginerie Chimică şi Protecţia Mediului

PREPARATION of HYBRID COATINGS with CONTROLLED WETTABILITY: Process Parameter Study

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Introduction/motivation

Renewable and **Environmentally Friendly** materials

Chitosan

→ *readily available, inexpensive, biodegradable*

Magnetite

→ *excellent way to resolve separation problems*

Hydrophobic coatings

Materials with **Hierarchical Morphology** and **Low Surface Energy**

Reference: *"Novel hybrid coatings with controlled wettability by composite nanoparticle aggregation"* (under review)

Objectives and Outline

Main objective: The aim of this paper is to investigate the effect of the variables that influence the wetting angle and the coating morphology on promising hybrid films with structured roughness for water repellent applications.

- Synthesis/characterization of coating components
- Hybrid thin film preparation
- The effects of the process parameters
- Conclusions and future work

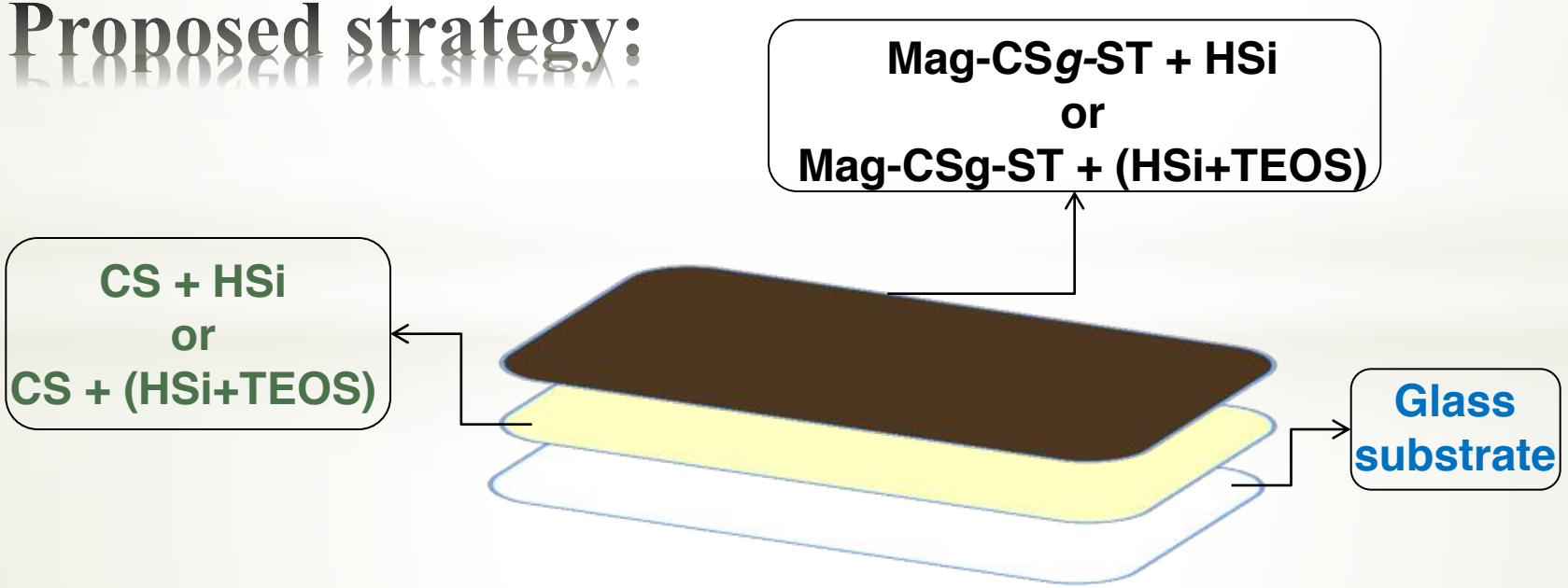
Coating components:

Ist - Polymeric binder: Chitosan (CS)

IInd - Coupling agent: Hexadecyltrimethoxy silane (HSi) or/and Tetraethyl orthosilicate (TEOS)

IIIrd - Composite particles: Magnetic-chitosan g-styrene (Mag-CS*g*-ST)

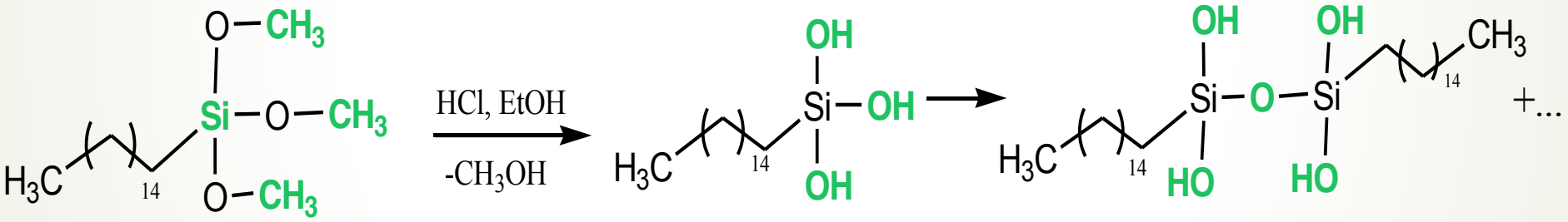
Proposed strategy:



I[st] – Chitosan dissoved in 1M acetic acid (CS).

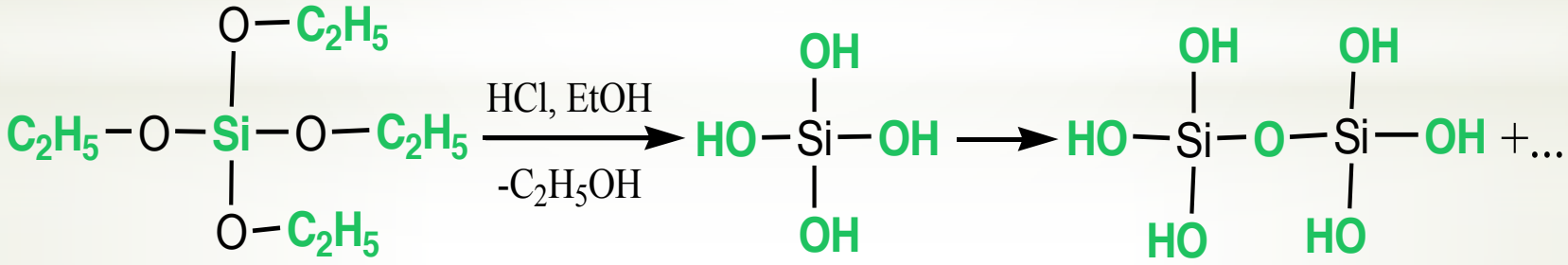
II[nd] – Coupling agent

a) Hexadecyltrimethoxy silane hydrolysis (HSi)



Reference: Spirk et al., Carbohydrate Polymers 93 (2013) 285–290.

b) Tetraethyl orthosilicate hydrolysis (TEOS)



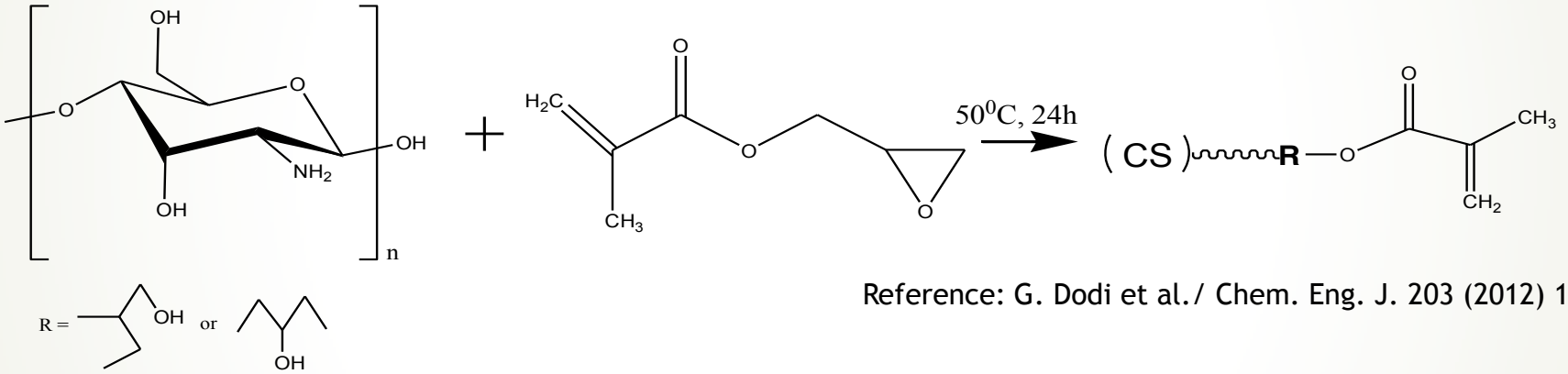
IIIrd – Composite particles

a) Magnetite nanoparticles preparation (Mag)

$$Fe^{2+} + 2Fe^{3+} + 8HO^{-} = Fe_3O_4 + 4H_2O$$

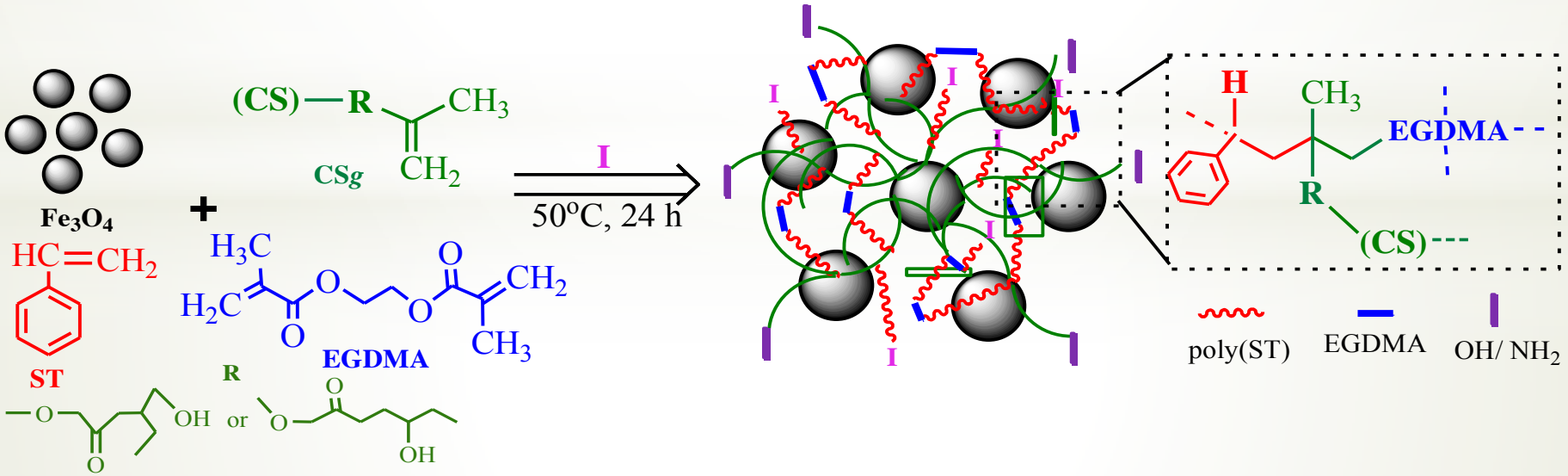
Reference: G.Dodi et al./J. Magn. Magn. Mater. 388 (2015) 49-58.

b) Synthesis of chitosan grafted with GMA (CSg)



Reference: G. Dodi et al./ Chem. Eng. J. 203 (2012) 130-141.

c) Composite particles synthesis (Mag-CSg-ST)



Characterization of composite particles(Mag-CS*g*-ST)

1. TEM

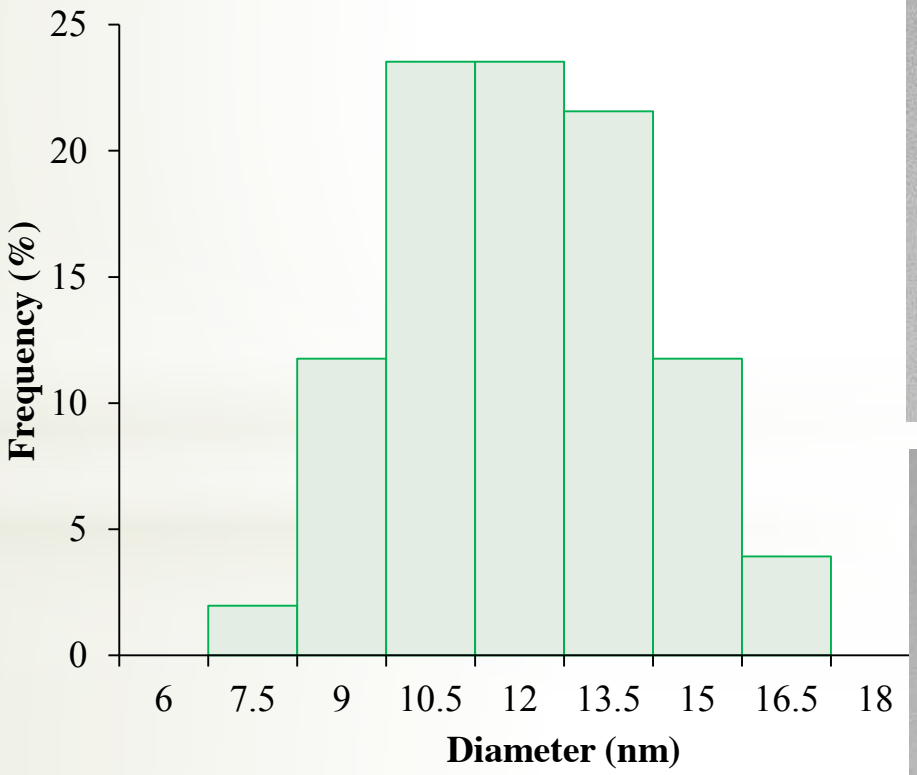


Figure 2. Size distribution histogram of Mag-CS*g*-ST

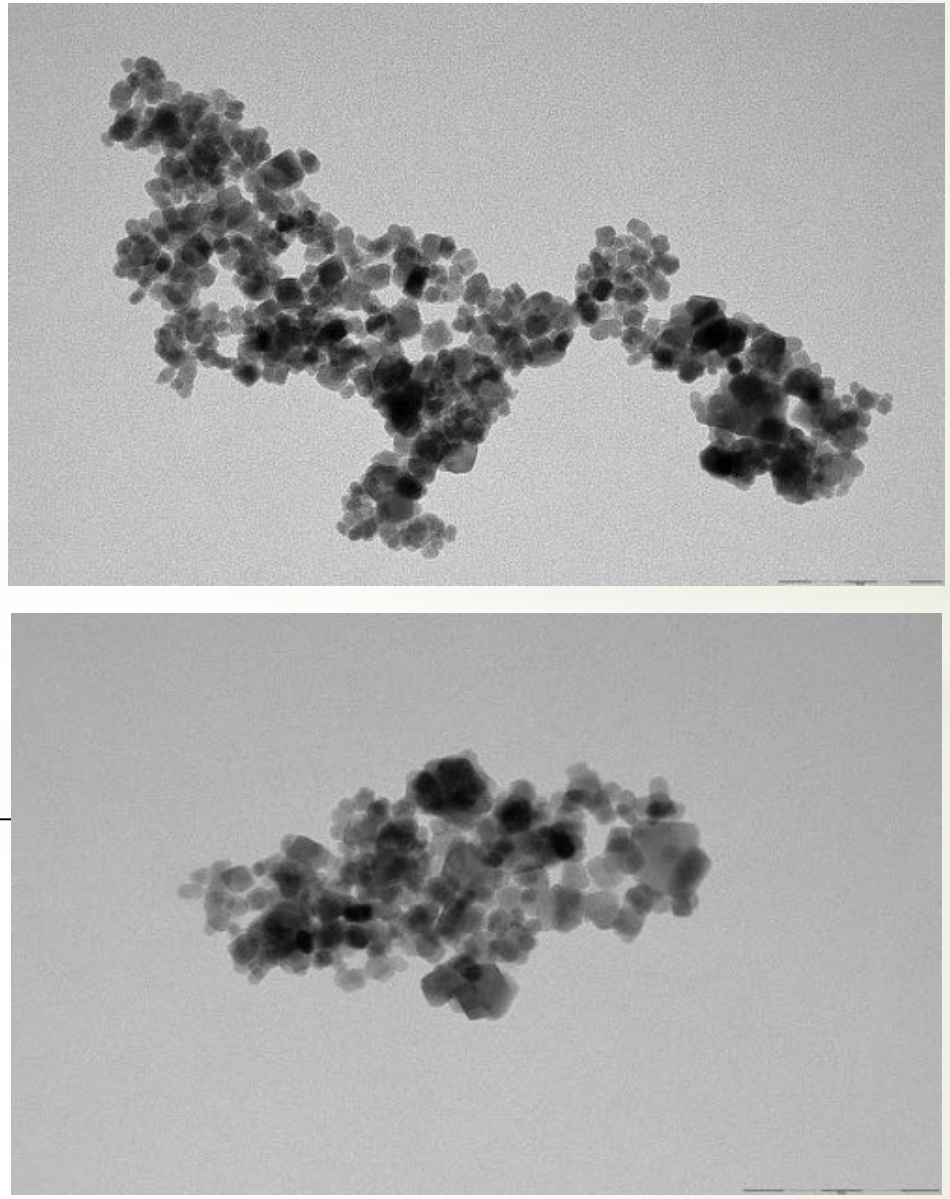
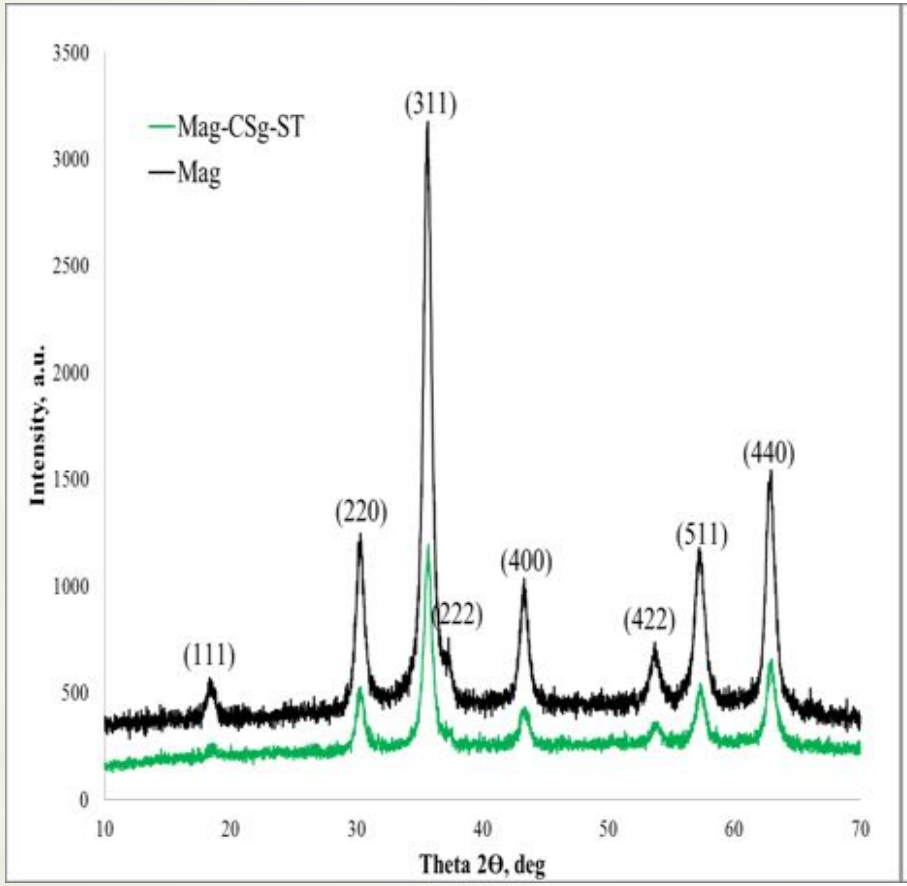


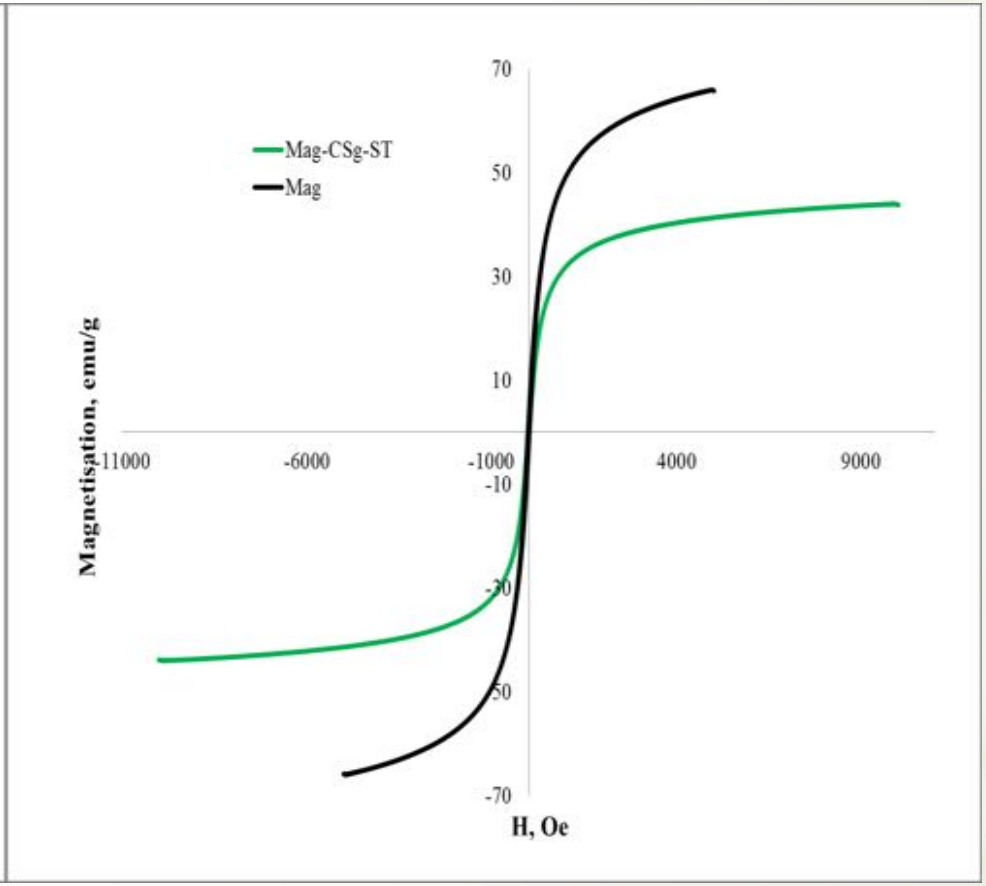
Figure 1. TEM pictures of Mag-CS*g*-ST

Characterization of composite particles(Mag-CSg-ST)

2. XRD



3. Magnetization

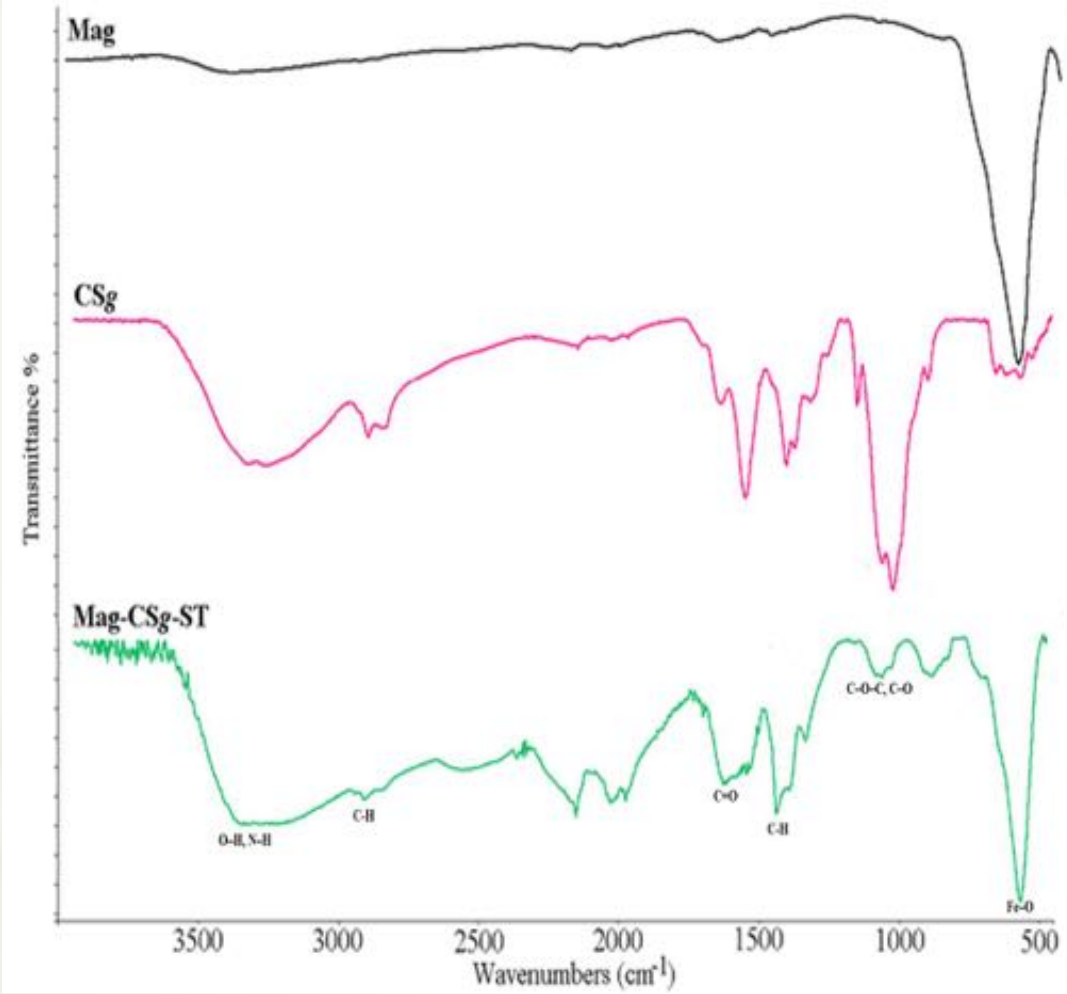


Material	Average size (TEM) (nm)	Size (XRD) (nm)
Fe_3O_4	13	9.17
Fe_3O_4-CS*g*-ST	11.65	10.64

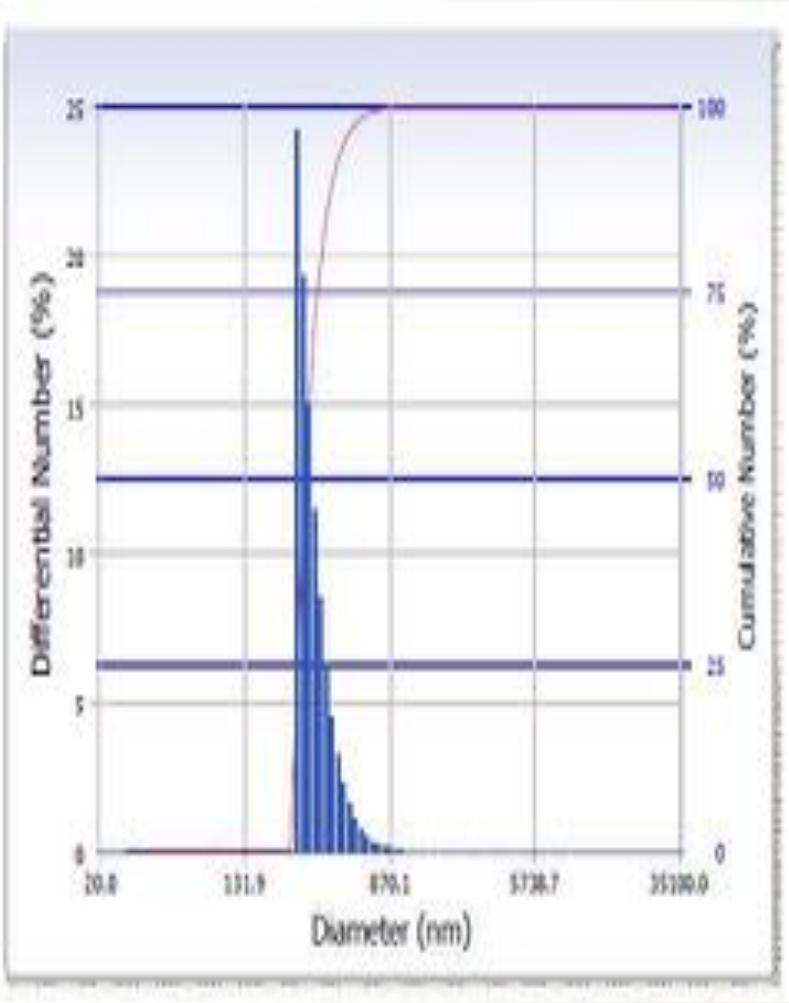
Batch	Magnetization, emu/g	Magnetite, % experimental
Mag	65.8	100
MagCS*g*ST	43.8	66.6

Characterization of composite particles(Mag-CSg-ST)

4. FTIR



5. DLS

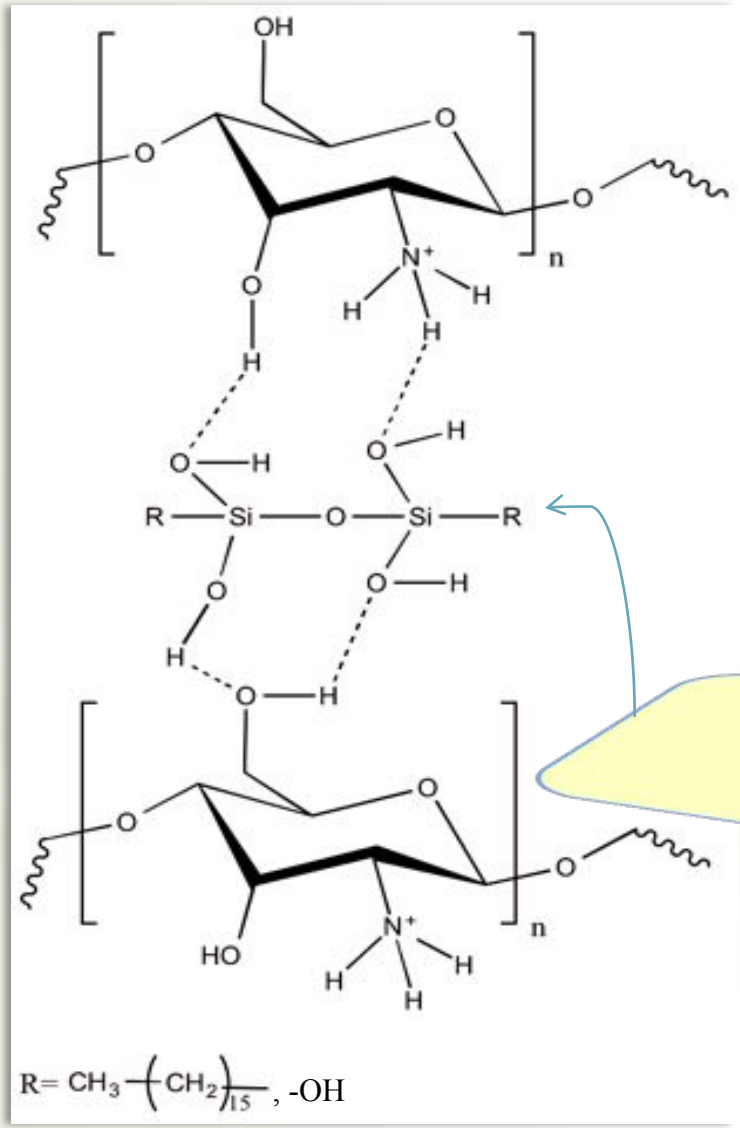


The chitosan, acrylates and styrene peaks are overlapped therefore, an exact estimation of chemical structure was not possible.

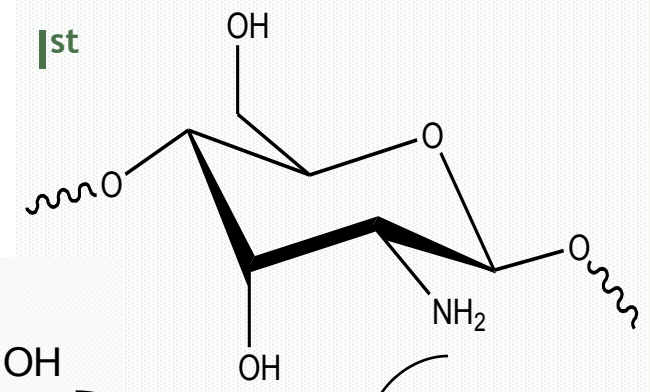
Size Mag-CSg-ST: 328 nm

Hybrid thin film preparation

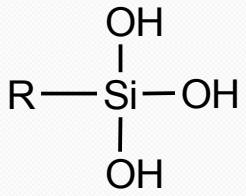
Layer 1



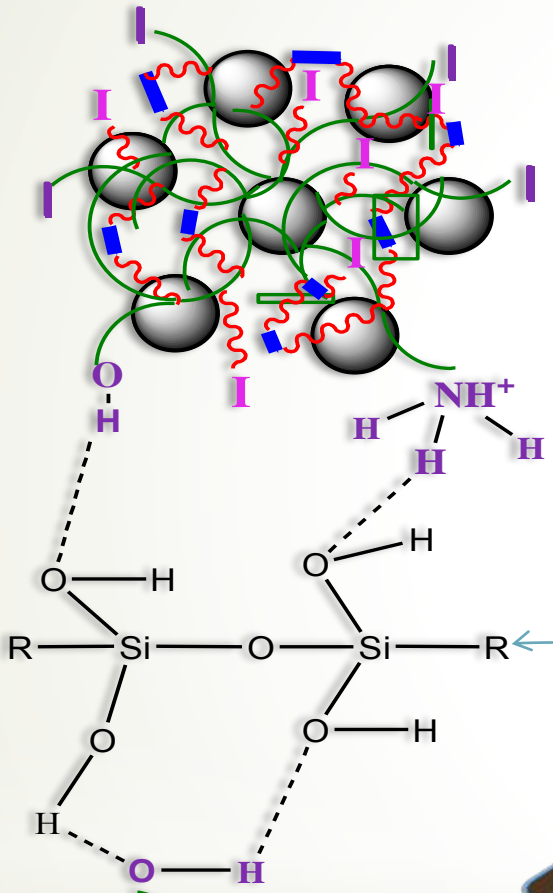
I st

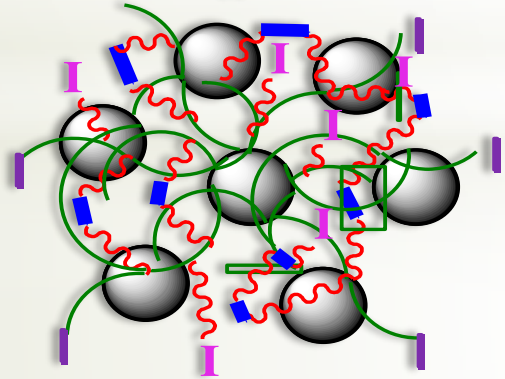


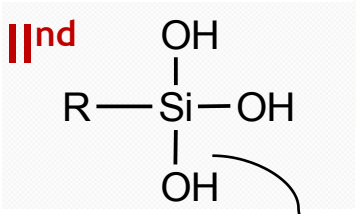
II nd

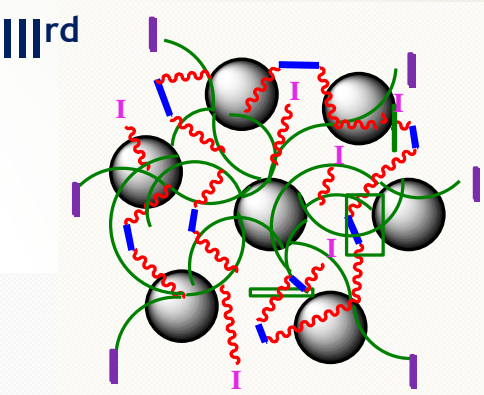


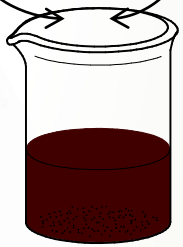
Layer 2











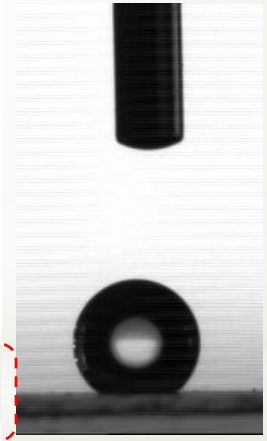
- Curing, treatment, rinsing

R= $CH_3-(CH_2)_{15}$, -OH

The effects of the process parameters

1. Coating composition and coating morphology

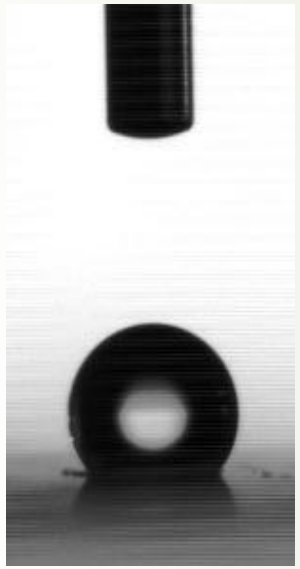
Plate	Mag-CS*g*-ST, %	CS, %	HSi, %	Wetting angle, ^{0}	Histerezis	Morphology
13	1	0	0.03	120.8	6.9	One layer, Spin coater
14	1	0.2	0.03	76	3.7	
15	1	0.5	0.03	79.9	3.7	
16	1	0.5	0.06	88.3	4.2	
34	1	1	0.03	91.7	2.8	
38	1	1	0.17	113.4	1.9	
54	**1.7**	**1**	**0.17**	**137.9**	**2.6**	**Layer by layer**
82	1.7	0	0.17	145.9		2 layers each



54 plate

2. Solvent in composite particle dispersion (IIIrd)

Plate	Solvent	Wetting angle, ^{0}	Histerezis
66	**water/ethanol mixture**	**140.1**	**1.5**
112	water	110.2	3.4
113	ethanol	110.4	4.4



66 plate

3. HSi hydrolysis time (IInd)

Plate	Time (h)	Wetting angle, ^{0}	Histerezis
109	24	121.5	2.2
110	48	120.6	2.3
92	68	119.1	1.9
66	**72**	**140.1**	**1.5**
118	96	115.6	2.7

4. HSi addition time before deposition (IInd)

Plate	Time	Wetting angle, ^{0}	Histerezis	Observation
141	15 h before deposition	112.6	2.6	drying 3min, 70^{0}C
133	**10 min. before deposition**	**122.7**	**0.7**	**drying 3min, 70^{0}C**

5. CS concentration (Ist)

Plate	CS conc., %	Wetting angle, ^{0}	Histerezis	Observation
145	0.5	105.3	2.3	drying 3min, 70^{0}C
146	0.75	100.8	2.9	drying 3min, 70^{0}C
147	**1**	**120.6**	**1.6**	**drying 3min, 70^{0}C**

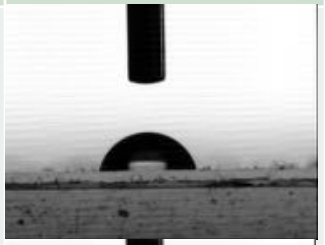
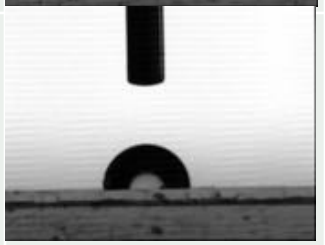
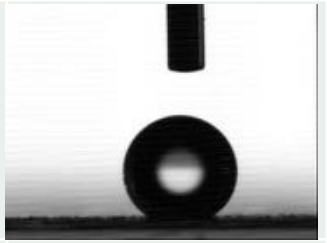
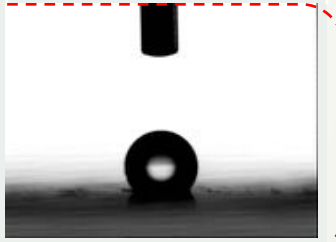
6. TEOS in silane mixture (IInd)

Plate	HSi (%)	TEOS (%)	Wetting angle, ^{0}	Histerezis
66	**100**	**0**	**140.1**	**1.5**
120	99	1	117.7	2.4
114	95	5	118.6	1.5
115	80	20	115.4	1.6
116	65	35	118.9	2.2
117	50	50	115.9	2.7

7. Layers drying conditions

Plate	Parameter	Wetting angle, ^{0}	Histerezis	Observation
129	**5min, 70^{0}C**	**124.7**	**1.1**	**two layers**
131	3min, 50^{0}C	120.2	1.6	two layers
130	3min, 50^{0}C	120.2	1.1	one layer
133	3min, 70^{0}C	122.7	0.7	two layers
134	3min, 70^{0}C	123.8	1	two layers, TEOS 1%
135	3min, 70^{0}C	115.5	2.6	two layers, silane old
148	3min 1st layer 4 min 2nd layer	113.1	1.9	RT after first CS layer, 70^{0}C after 2nd ; drying RT after first Mag layer

8. Wetting angle versus deposition method

Plate	Spin coater	Airbrush	
CS	78.2	78.1	
CS+SI	103.4	108.2	
Mag-CS*g*-ST +SI	120.8	146.9	
CS+HSi+ Mag-CS*g*-ST	88.3	101.4	
(CS+HSi)/ (Mag-CS*g*-ST+SI)	**122.4**	**140.1**	

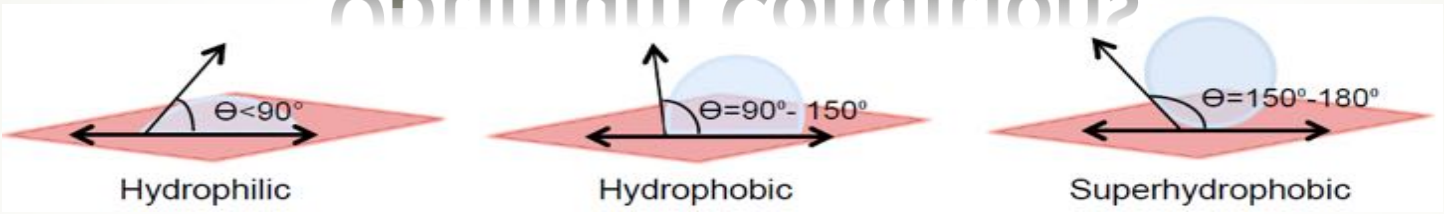
*Optimum conditions:

- ✓ Solvent in particle dispersion: water/ethanol mixture;
- ✓ HSi hydrolysis time: 72 h;
- ✓ No TEOS in silane mixture;
- ✓ HSi addition time: 10 minutes before deposition;
- ✓ Deposition method: layer by layer;

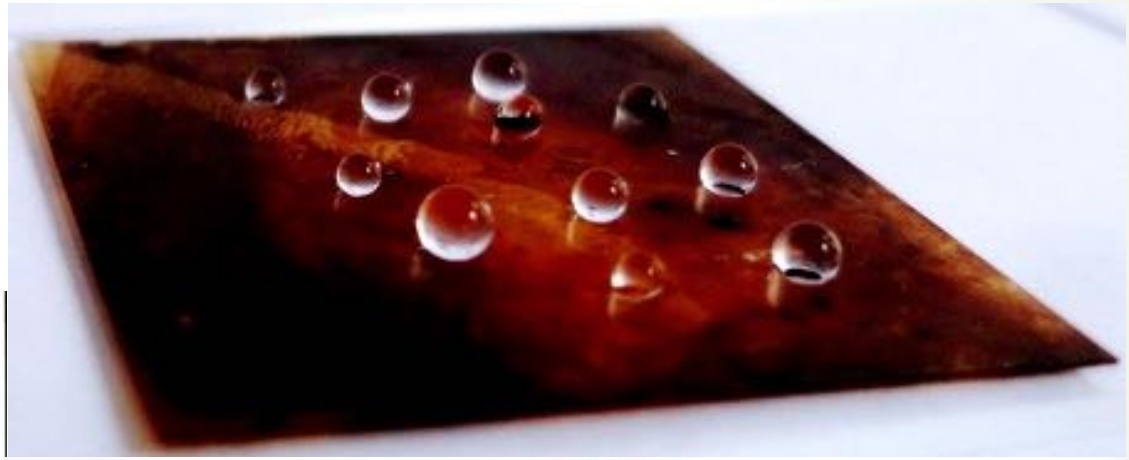
  Layer 1: 2 mL of CS 3% + 3.5 mL EtOH + 0.5 mL HSi

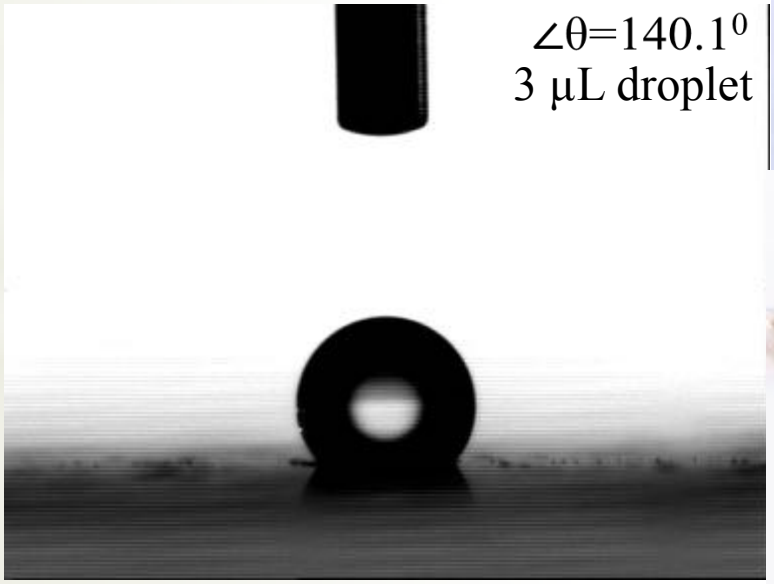
  Layer 2: 2.5 mL of Mag-CS*g*-ST 2% in water/EtOH mixure + 0.5ml HSi
- ✓ Layer intermediate drying: with drying between layers 5 min. at 70^0C;
- ✓ Plate is dried overnight at 70^0C;
- ✓ The plate is then treated with 0.6% ammonia solution, rinsed and dried overnight again at 70^0C.

Contact Angle and Non-Wetting Properties in Optimum Conditions

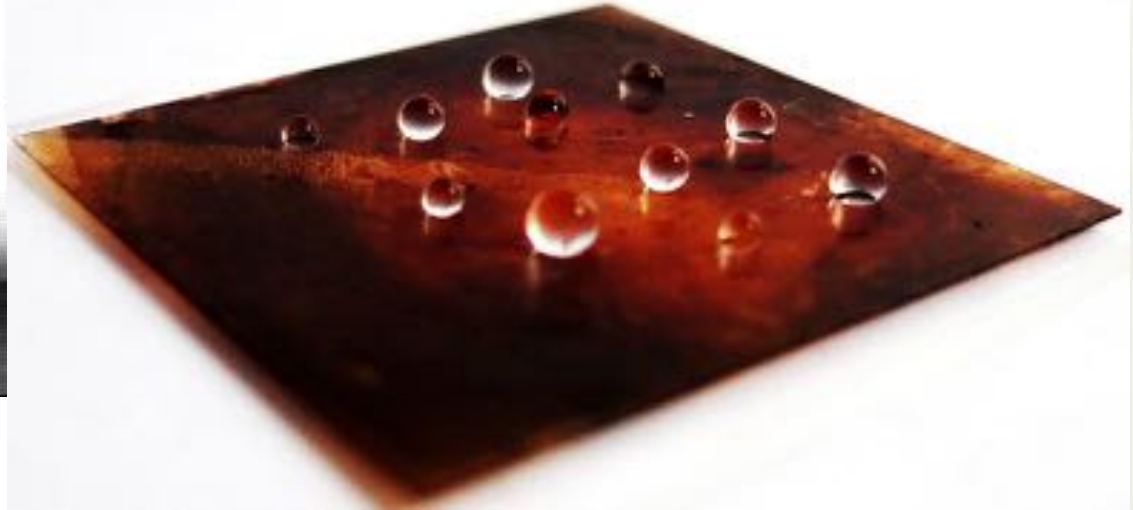


66 Plate Pictures



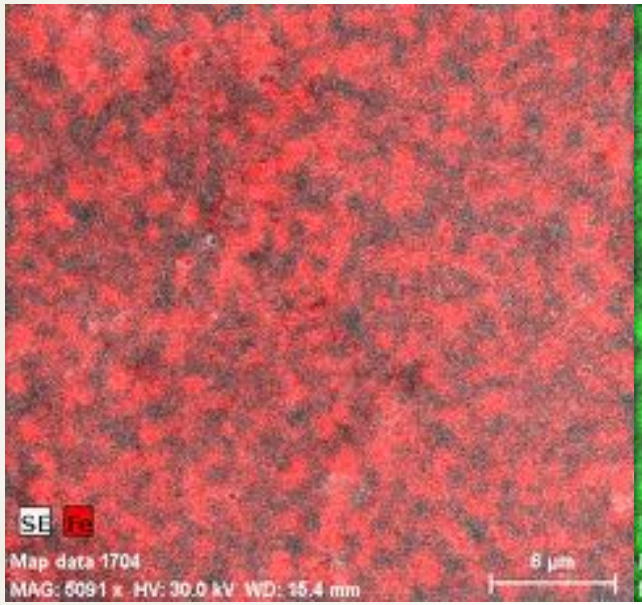


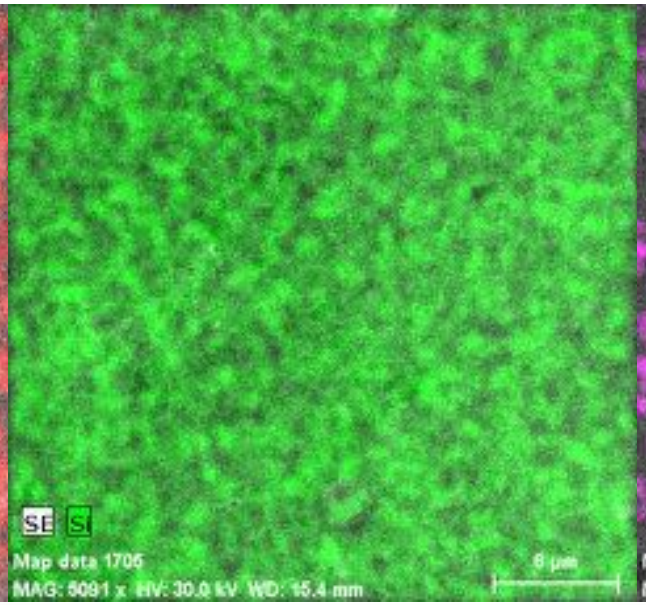
$\angle\theta=140.1^0$
3 μL droplet

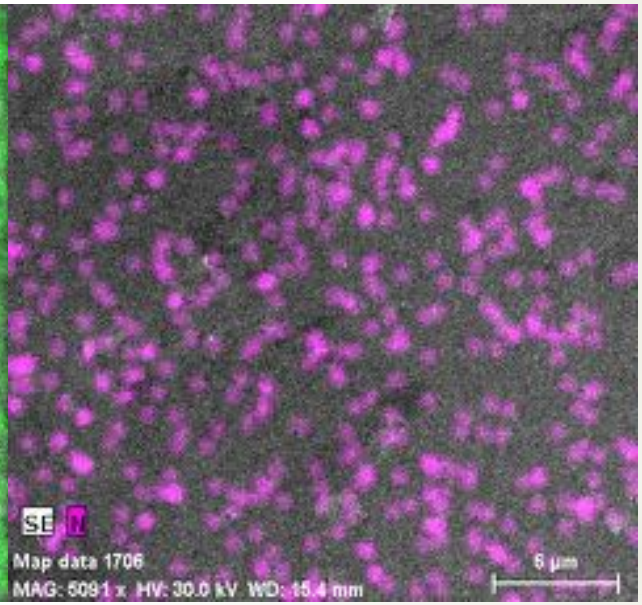


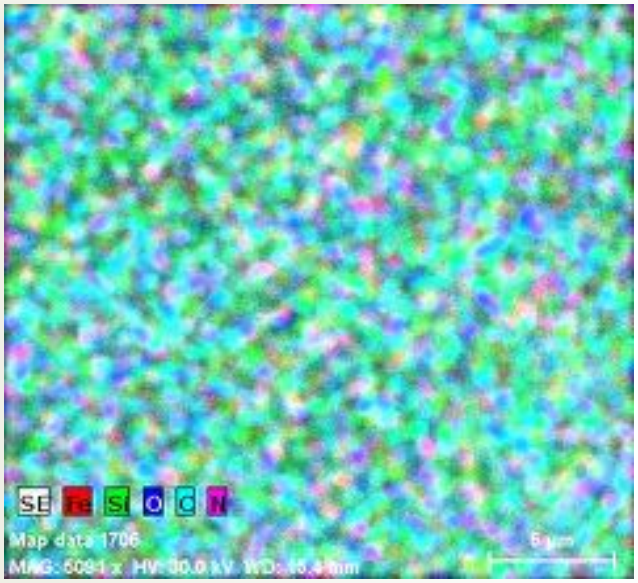
Characterization of optimum coating

1. EDX





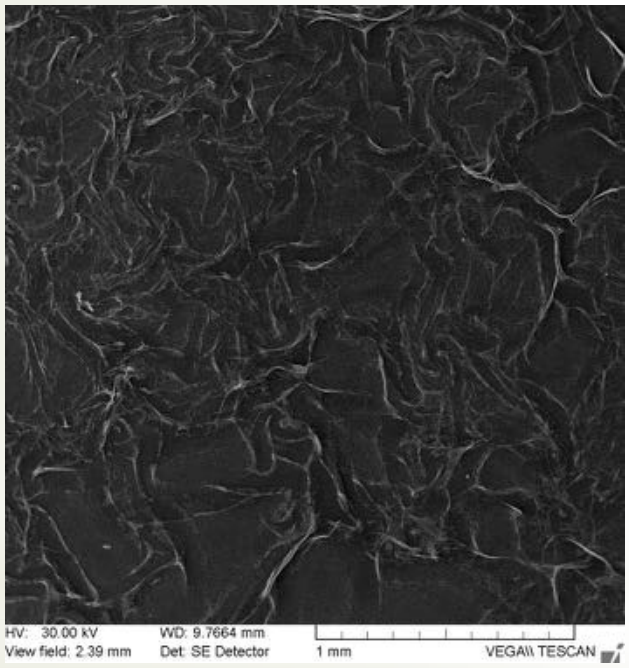


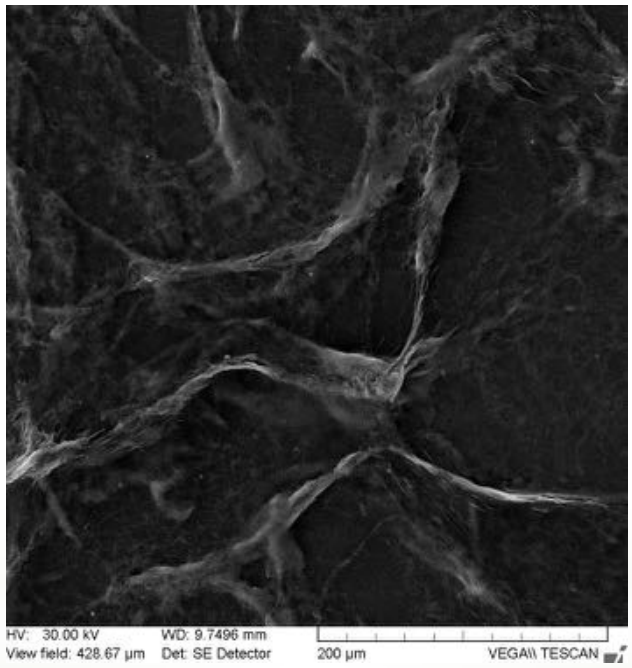


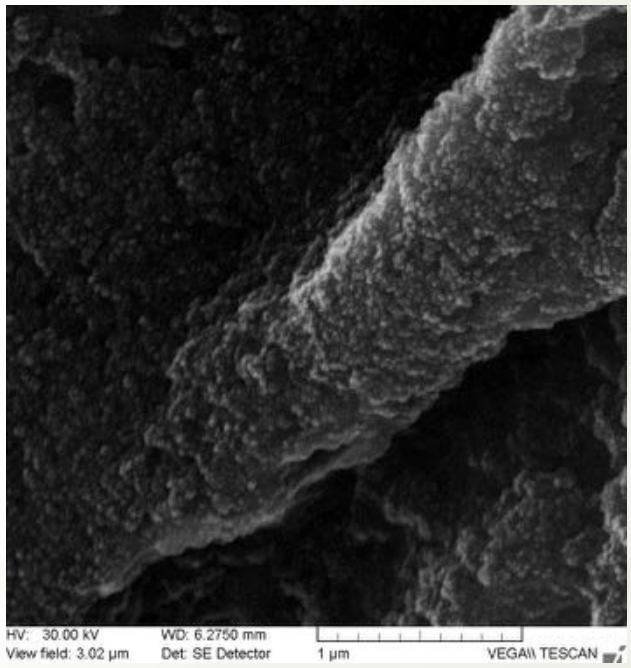
Element	Weight, %	Normalized, %
Oxygen	53.11	61.85
Silicon	21.6	25.15
Nitrogen	5.16	6.01
Carbon	2.79	3.24
Iron	3.21	3.73

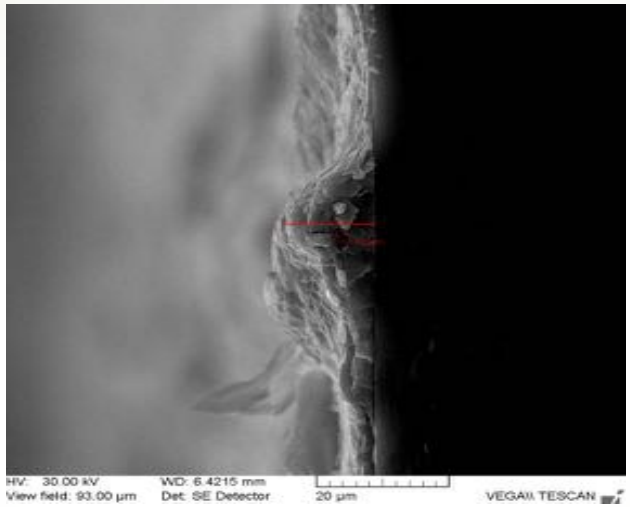
Characterization of optimum coating

2. SEM









SEM micrographs of hybrid coating CS+Si/MagCSgST+Si (66 plate)

Conclusions and future work

- Magnetic chitosan grafted styrene particles were synthesized, characterized and successfully evaluated for the hybrid film preparation.

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- The effects of various parameters were studied and reproducibility was improved.
- The ability of the composite particles to generate patterned films with hierarchical roughness and controlled wettability was demonstrated.
- The water contact angle measurements evidenced hydrophobic surfaces.

Future work: test ice-repellent properties.

Acknowledgements

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THANK YOU FOR YOUR ATTENTION!