CNES Presentation

Development of a regenerative sensor in micro- and nano-technologies for the detection and the quantification of traces of specific molecules (NanoTRAACES)

08/08/2018

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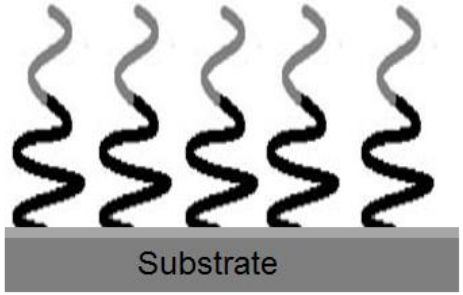
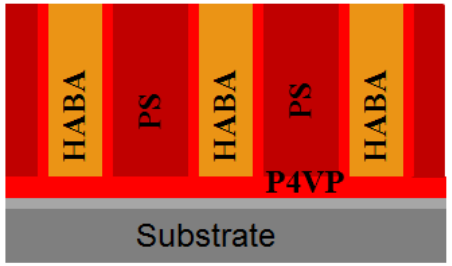
I/ Reminder of the conception of the active part of the sensor

- *Control of the copolymer organization on substrates:*

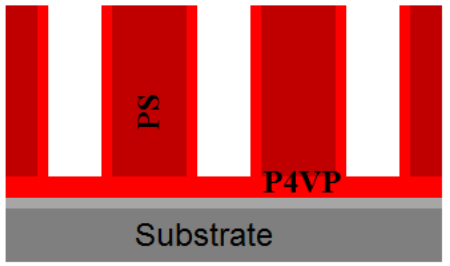


1) Deposition by dip-coating

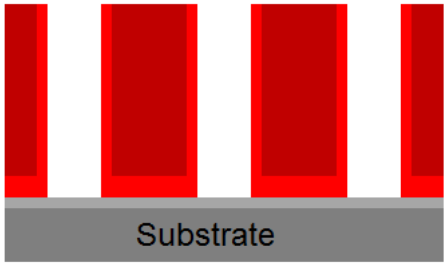
2) Annealing under 1-4, dioxane vapors

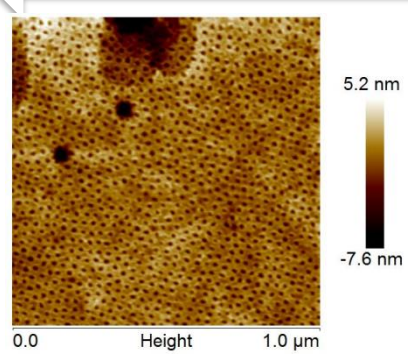


Rising in Methanol



UV, Plasma Ar



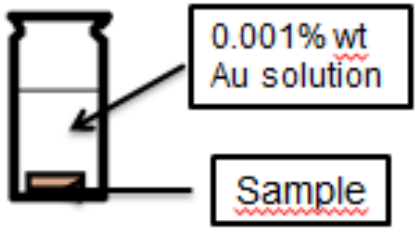


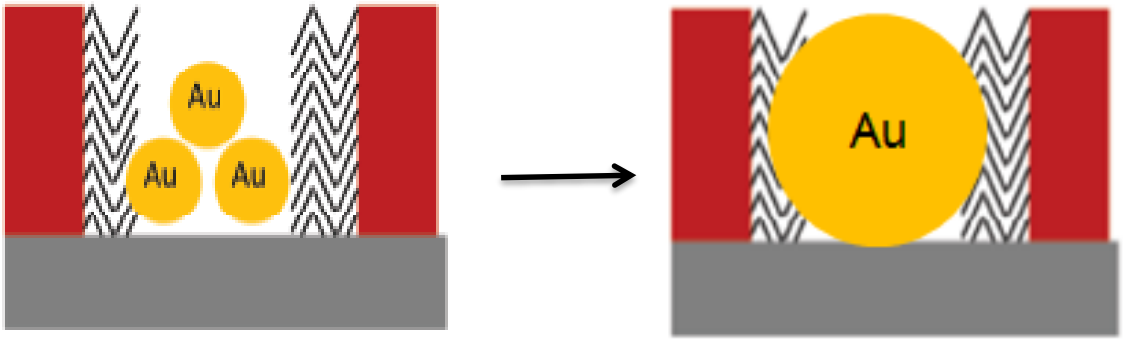
Formation of cylindrical nanopores

I/ Reminder of the conception of the active part of the sensor

- *Growth of Au nanoparticles (seeds):*

Pre-treated silicon wafers or stainless steel plates *(surface treatment, copolymer deposition + UV + Plasma Ar)*
0.001 % gold colloidal solution for 1 hour at room temperature





Adsorption of Au^{3+} ions on the NH_2 of the PS-P4VP

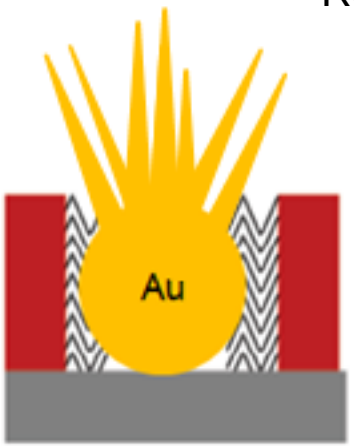
Reduction of Au^{3+} ions by **hydrate of hydrazine (5 min)**

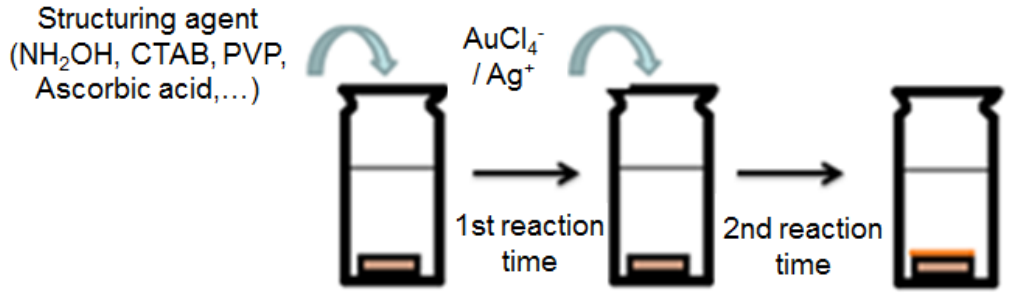
I/ Reminder of the conception of the active part of the sensor

- *Growth of flower-like structures – wet chemical way:*

Structuration by a structuring agent:

- Substrates immersion in **the structuring agent aqueous solution for 45 min**
- Addition of a metallic colloidal solution
- Reaction without stirring for **one hour**





$$t_{immersion} = (t_{structuring\ agent}) + (t_{gold\ colloidal\ solution}) + (t_{refeeding})$$

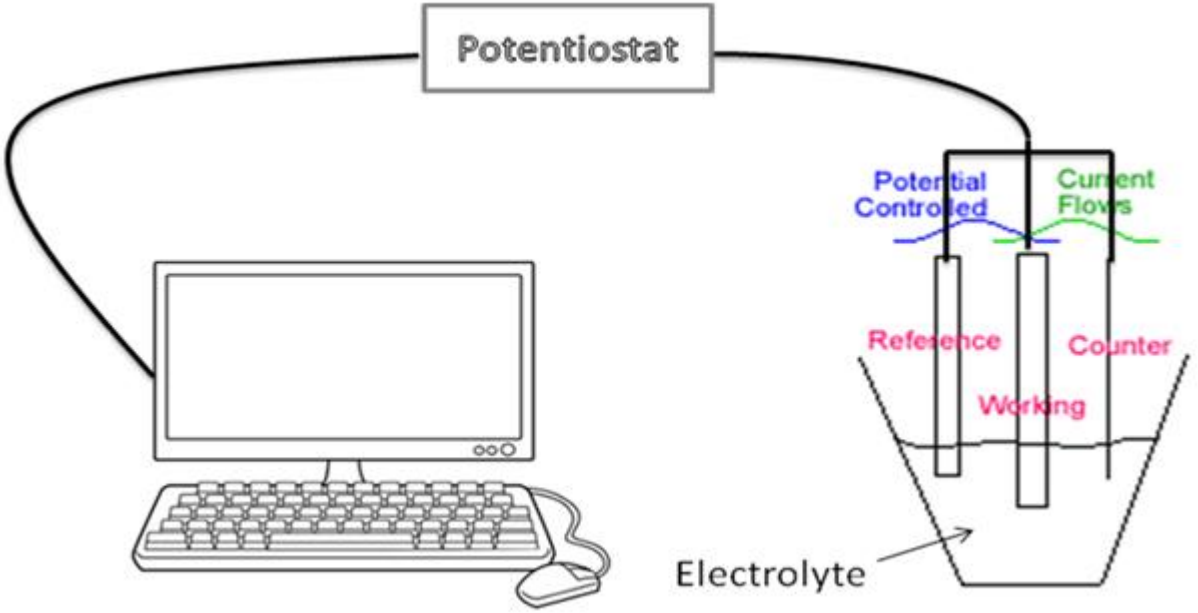
1st reaction time — 2nd reaction time

Temperature
pH-Kinetics-structuring agent

I/ Reminder of the conception of the active part of the sensor

- *Growth of flower-like structures– electrochemical way:*
  - Electrodeposition of metallic nanostructures onto **stainless steel plates pre-patterned with PS-P4VP and gold seeds**
  - Working electrode = sample - Reference electrode Ag/AgCl - Counter electrode = Pt

D-L. Zhou, R-Z. Wang, M. Zhang, X. Weng, J-R. Chen, A-J. Wang, J-J. Feng, Electrochemica Acta (2013), 108, 390.



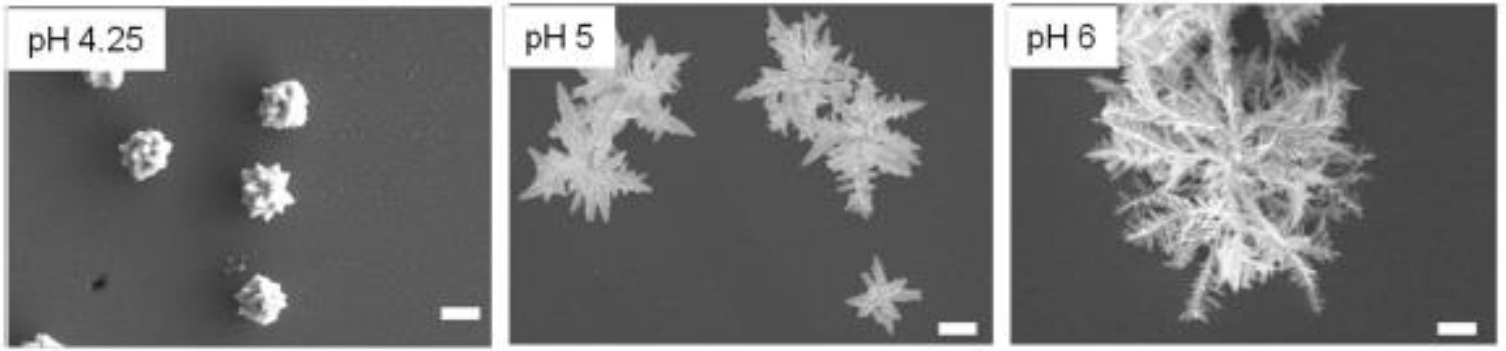
Temperature
pH-Kinetics- Electrolysis potential

I/ Reminder of the conception of the active part of the sensor

- *Control of physico-chemical parameters on growth process*
  - ***Temperature:*** Insulated closed double jacketed glass cell – blank with water

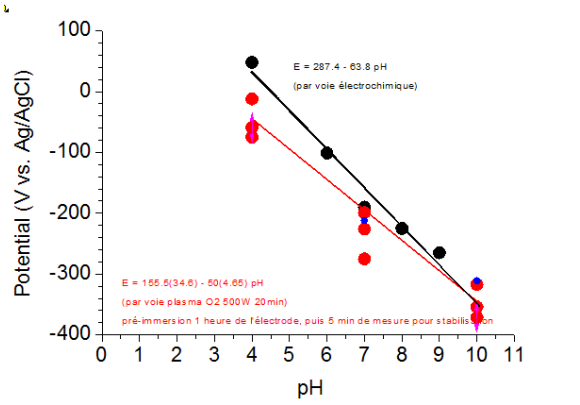
  - ***pH***: Control by pH-meter of the structuring agent aqueous solution

Z. Wang, M.S. Bharathi, R. Hariharaputran, H. Xing, L. Tang, J. Li, Y-W. Zhang, Y. Lu, ACS Nanoletters (2013), 7, 2258.



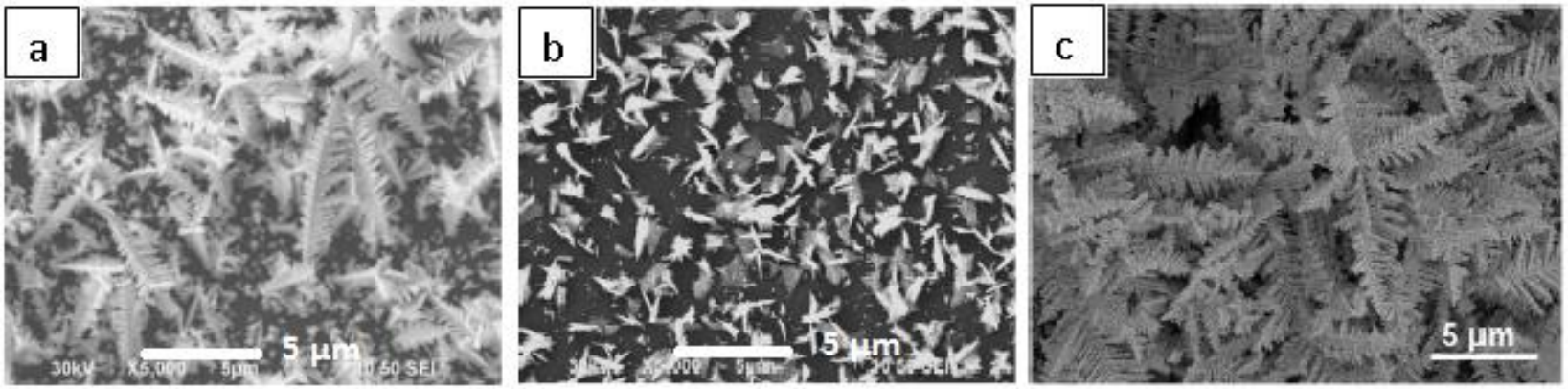
SEM images of Au nanodendrites prepared by chemical way. Scale bar: 2 µm.

Other method: Calibration of a W µ-electrode to measure the pH of the solution during the entire reaction



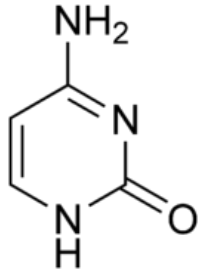
I/ Reminder of the conception of the active part of the sensor

- *Growth mechanism of **Au** dendritic nanostructures*
  - *Structuring agent + morphology of seeds + parameters*

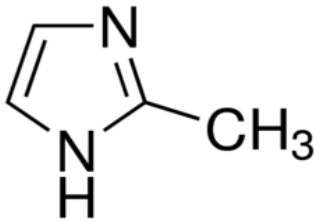


SEM images of Au nanodendrites prepared by electrodeposition process. Scale bar: 5µm.

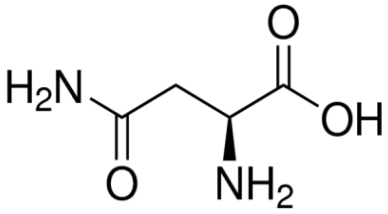
Cytosine (a) N-methylimidazole (b) L-asparagine (c)



Z-Y. Lv, L-P. Mei, W-Y. Chen, J-Y. Chen, A-J. Wang, Sensors and Actuators B (2014), 201,92.



J-J. Feng, Z-Y. Lv, S-F. Qin, A-Q. Li, Y. Fei, A-J. Wang, Electrochimica Acta (2013), 102, 312.



Z-Y. Lv, A-Q. Li, Y. Fei, Z. Li, J-R. Chen, A-J. Wang, J-J. Feng, Electrochimica Acta (2013), 109, 136.

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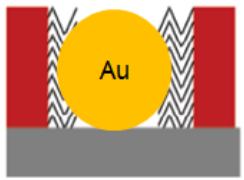
II/ Synthesis of Au flower-like structures: Formation growth process

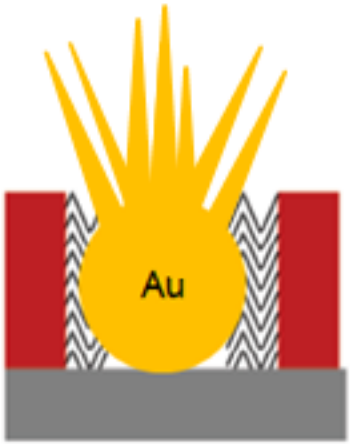
1) *Control of the copolymer organization on substrates:*
2) *Growth of Au nanoparticles (seeds)*

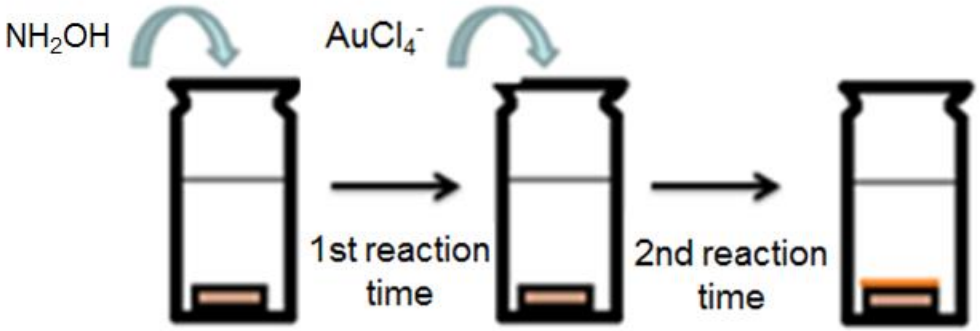


3) *Growth of Au flower-like structures– wet chemical way:*

Structuration by NH_2OH as structuring agent:

- Substrates immersion in **NH_2OH aqueous solution (20mM) for 45 min**
- Addition of a Au colloidal solution (1% wt)
- Reaction without stirring for one hour

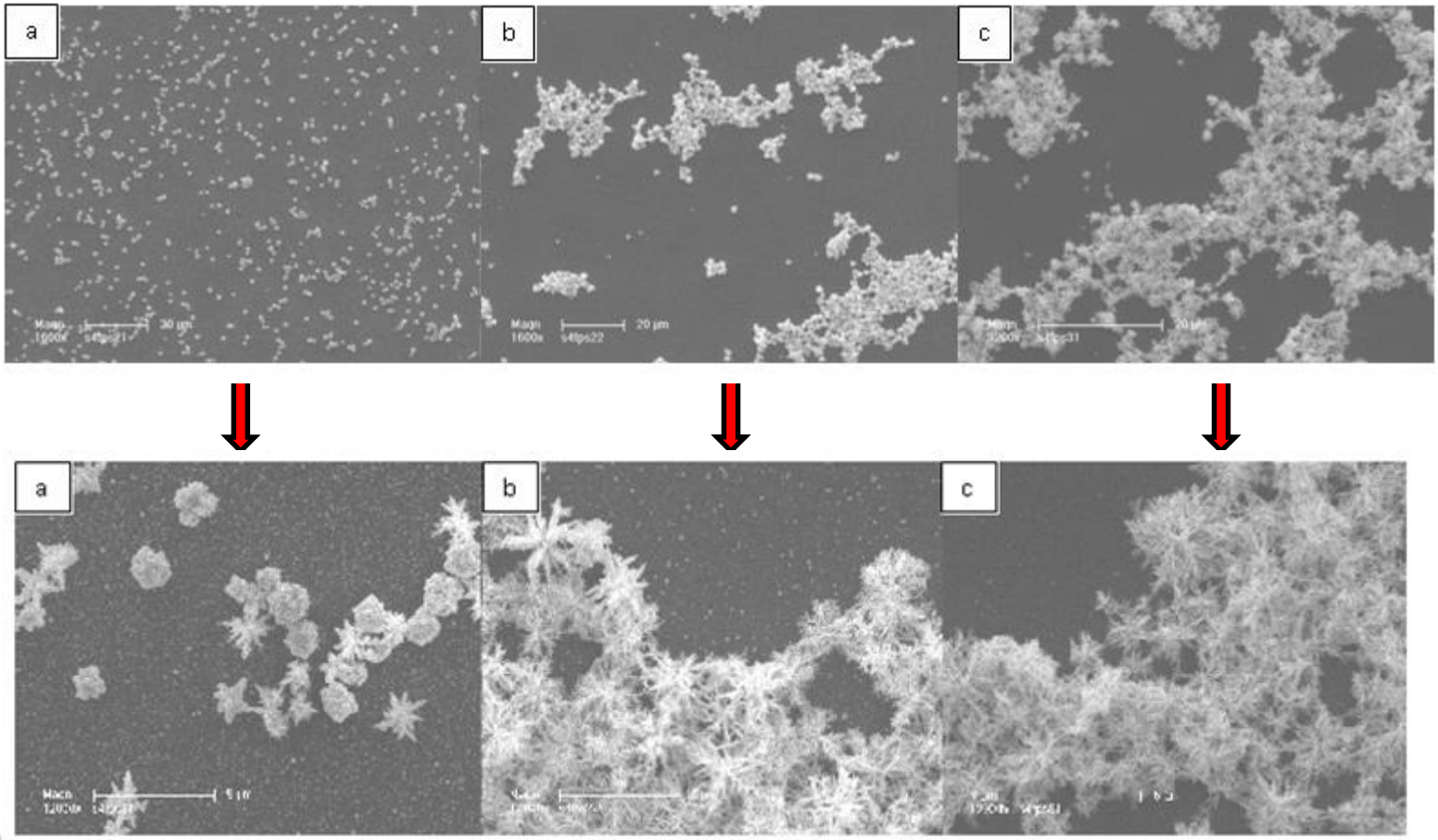




II/ Synthesis of Au flower-like structures: Study of main parameters

Parameters :
Si / PS-P4VP + Seeds
$[HAuCl_4]$ = 1%
Room temperature
No refeeding
No stirring
$t_{immersion}$ = 1h45

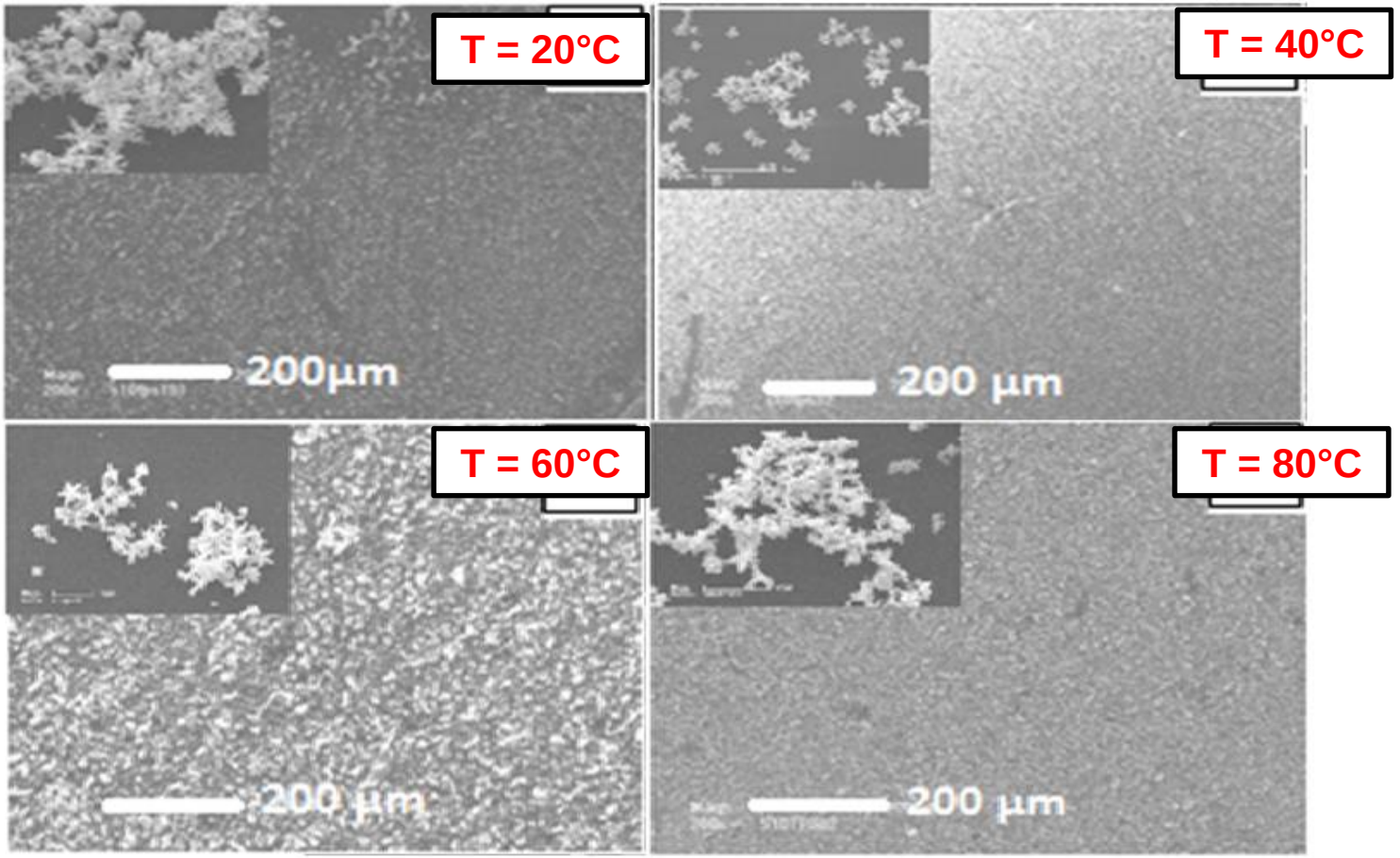
- *Effect of growth solution pH onto structures*



II/ Synthesis of Au flower-like structures: Study of main parameters

Effect of temperature control on silicon wafers: Reproducibility

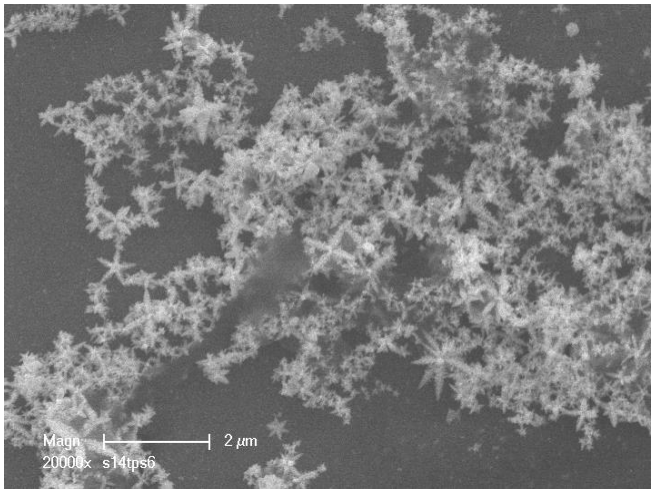
Parameters :
Si / PS-P4VP + Seeds
$t_{immersion}$ = 1h45
$[HAuCl_4]$ = 1%
pH_{NH_2OH} = 5,5
without agitation
without refeeding

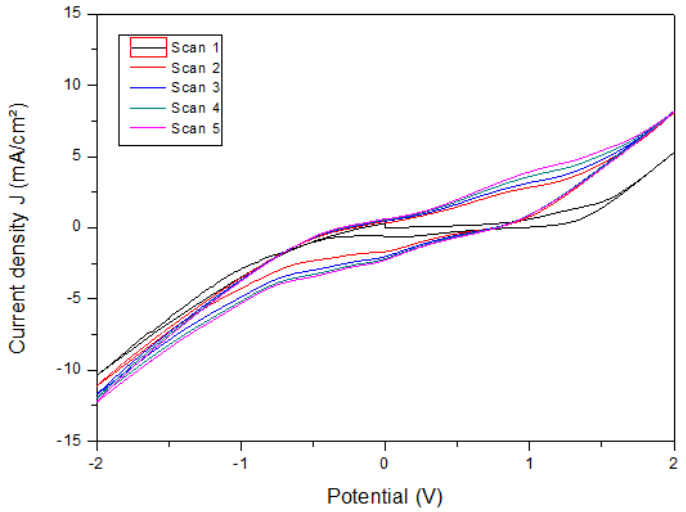


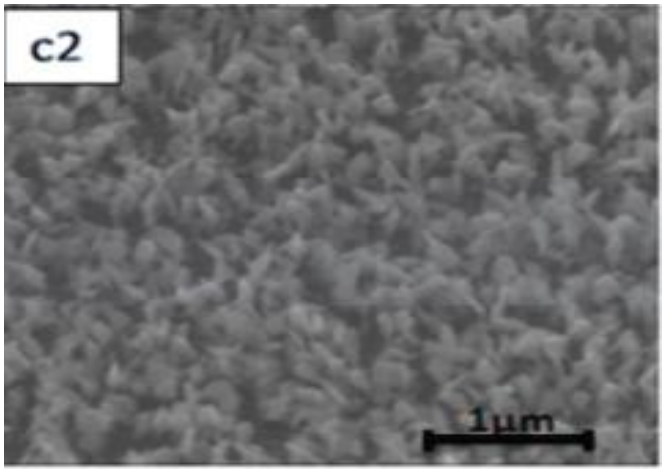
SEM images of Au flower-like structures prepared at different temperatures.

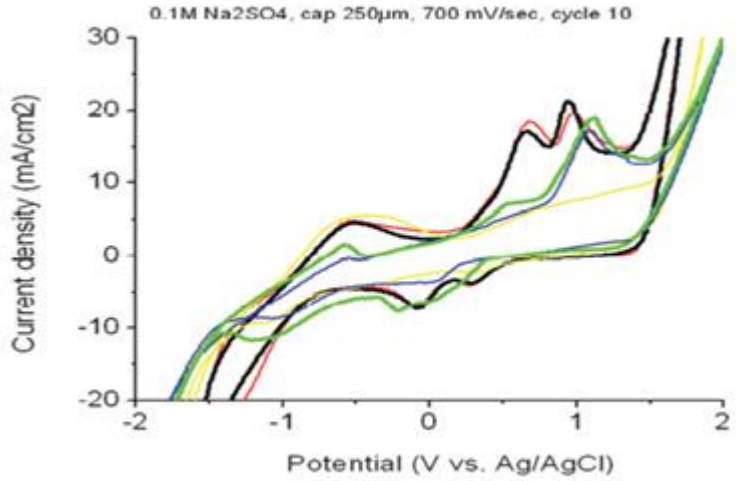
II/ Synthesis of Au flower-like structures: Optical and electrochemical properties

- *Study of electrochemical activities*









SEM image of stainless steel sample with gold NPs /Ag NPs and cyclic voltammograms (0.1 M Na_2SO4, 50 mV/s, cycle 5)

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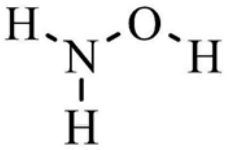
III/ Synthesis of Ag flower-like structures: Chemical way: different structuring agent

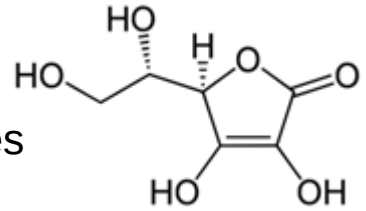
- NH_2OH structuring agent
  - Solution-based reduction with $AgNO_3$ as the precursor



T. Yang, Y. Han, J. Li, Chemical Engineering Science (2015), 138, 457.

$$Ag^+ + 2NH_2OH \rightarrow 2Ag + 2H_2O + N_2 + 2H^+$$

- Ascorbic acid structuring agent
  - Most popular reducer to form metallic flower-like structures

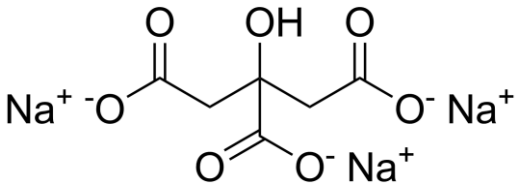


- Citrate structuring agent
  - 2 solutions procedure
    - Solution A
    - Solution B

Control of T and pH
Strong stirring

→ Flower-like structures

Mohammad RAJAB, Thesis (2013), UHA.

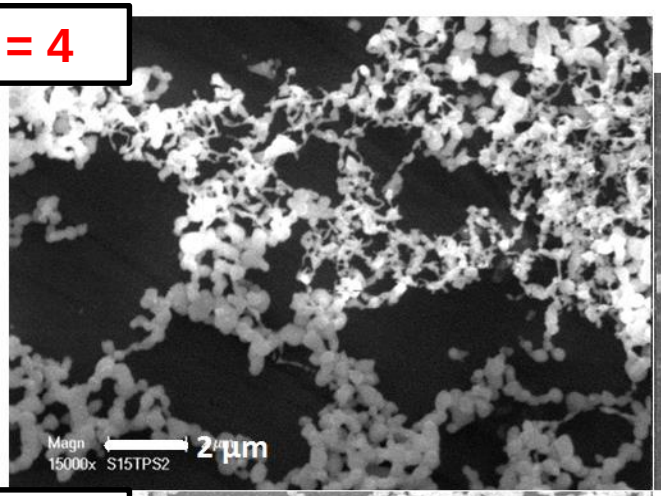


III/ Synthesis of Ag flower-like structures: Chemical way: NH_2OH

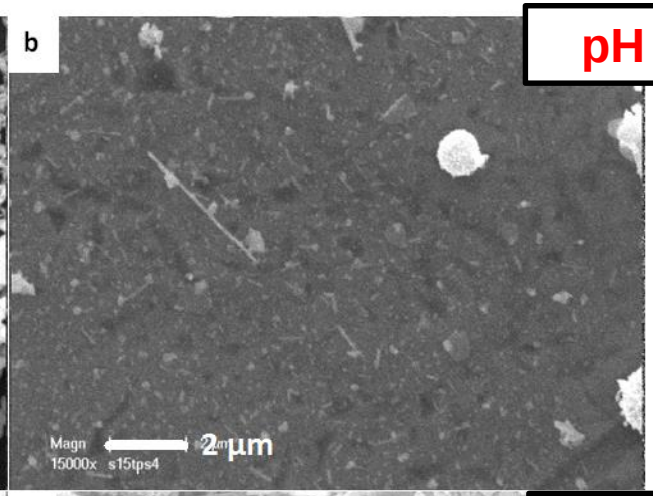
Parameters :
Ac / PS-P4VP + Seeds
$t_{immersion}$ = 1h45
$[AgNO_3]$ = 10 mM
T = 30 °C
without agitation
without refeeding

- *Effect of growth solution pH onto structures*

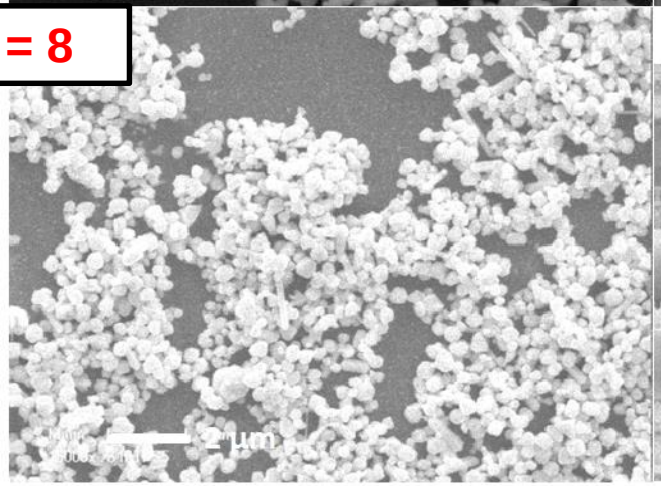
pH = 4



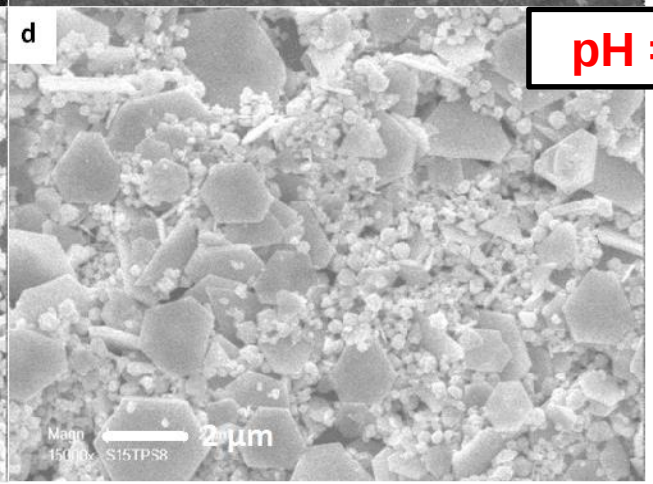
pH = 6



pH = 8



pH = 10



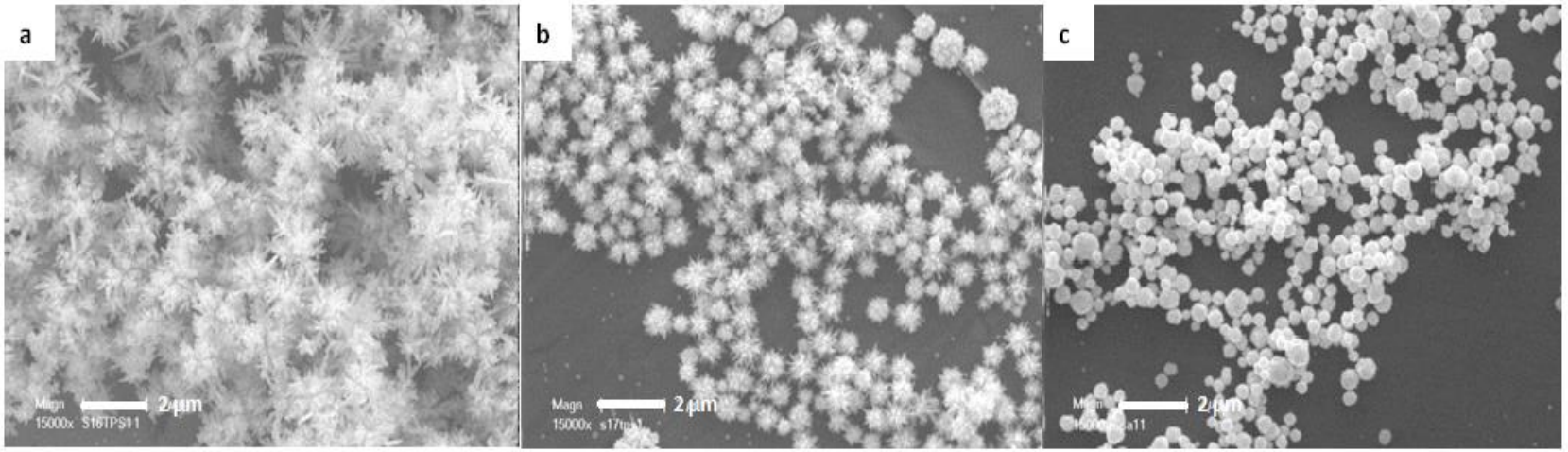
SEM images of Ag flower-like structures prepared at different pH.

III/ Synthesis of Ag flower-like structures: Chemical way: Ascorbic acid

Parameters :
Ac / PS-P4VP + Seeds
$t_{immersion}$ = 1h45
$[AgNO_3]$ = 10 mM
T = 30 °C
without agitation
without refeeding

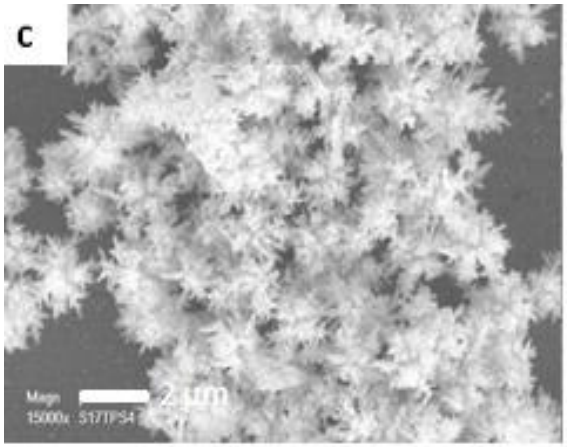
- *Effect of growth solution pH onto structures*

pH = 3 **pH = 5** **pH = 7**



SEM images of Ag flower-like structures prepared at different pH.

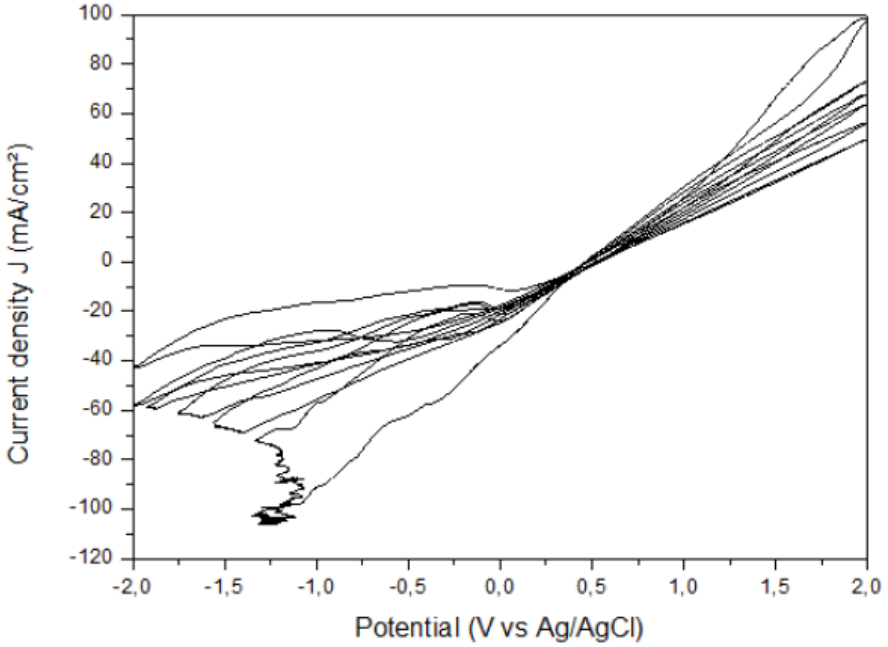
pH = 4



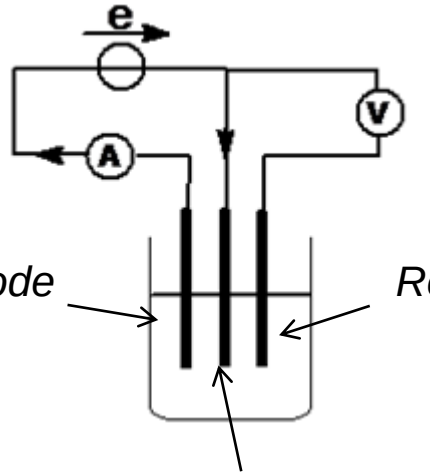
III/ Synthesis of Ag flower-like structures: Electrochemical way

- Three-electrode device
  - Electrodeposition process

⇒ Fast reduction of Ag^+ ions on the working plate
⇒ Control of pH
⇒ Control of electrolysis potential and process time
⇒ Room temperature



X. Qin, Z. Miao, Y. Fang, D. Zhang, J. Ma, L. Zhang, Q. Chen, X. Shao, Langmuir (2012), 28, 5218.



Counter electrode of Pt

Reference electrode of Ag/AgCl

Working electrode (sample)

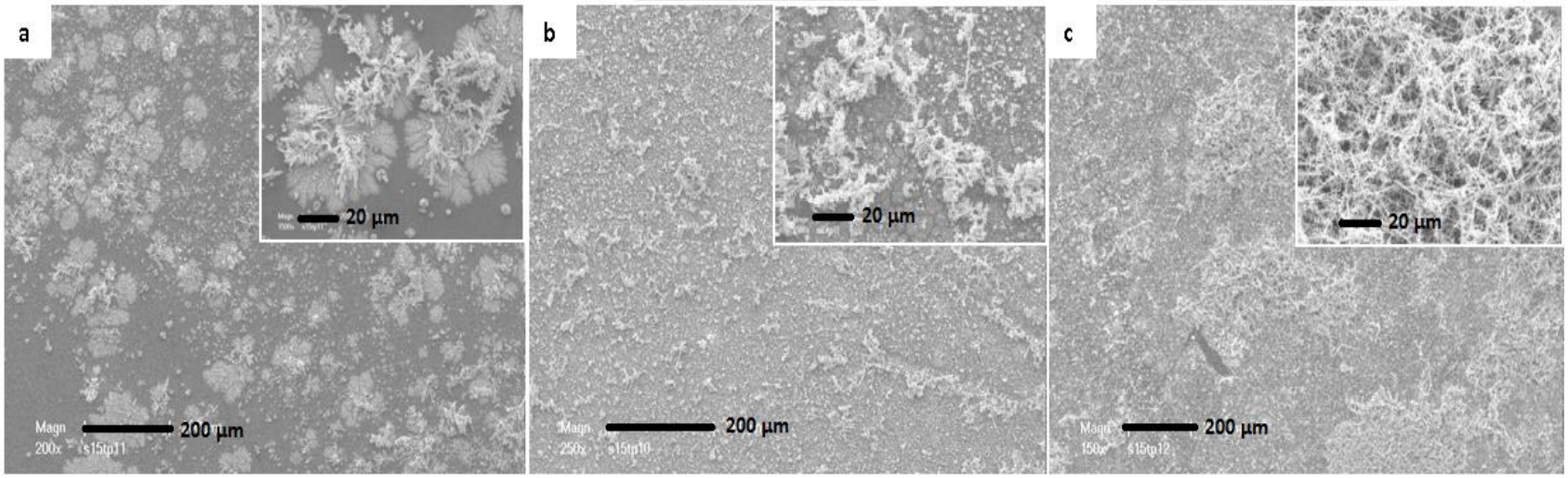
Electrolyte = $AgNO_3$ aqueous solution

III/ Synthesis of Ag flower-like structures: Electrochemical way

Parameters :
Ac / PS-P4VP + Seeds
[$AgNO_3$] = 10 mM
$t_{electrolysis}$ = 300s
Room Temp
pH = 10
without agitation
without refeeding

- *Effect of electrolysis time on Ag dendritic structures*

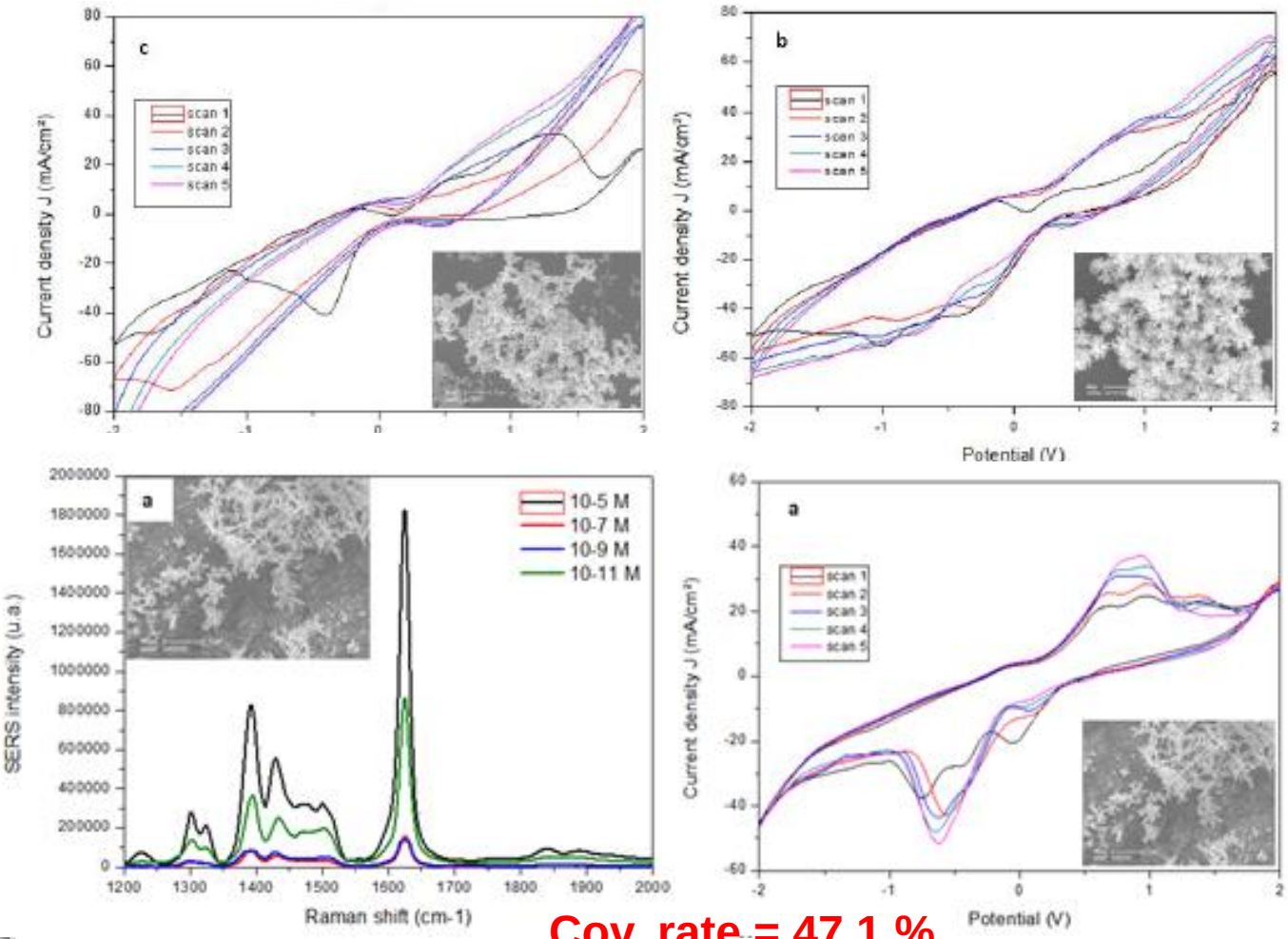
E = -0.5 V | **E = -1 V** | **E = -1.5 V**



SEM images of Ag dendritic structures prepared at different electrolysis potential

III/ Synthesis of Ag flower-like structures: Electrochemical measurements

- *Study of electrochemical activities*



Na_2SO_4 (0.1 M) aqueous solution Cyclic voltamperometry at 200 mV/s over 5 cycles.

Cov. rate = 47.1 %

Cyclic voltametry of Ag nanospheres, nanoflowers and nanodendrites

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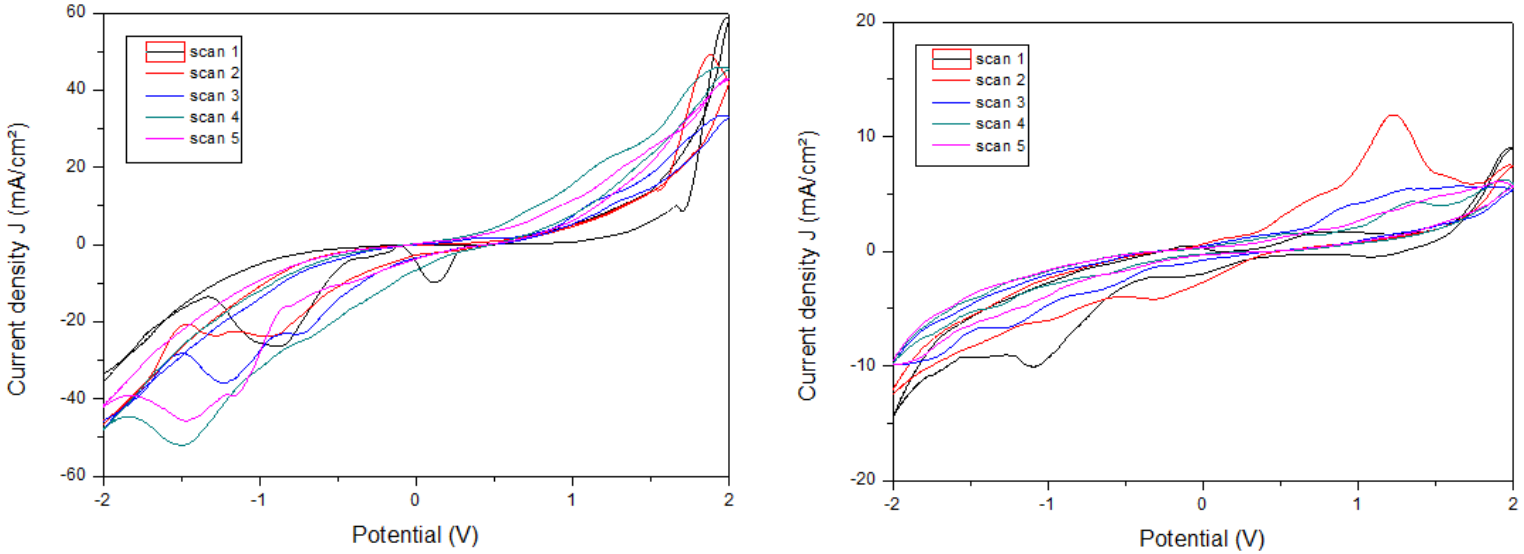
IV/ A new route: Bimetallic Ag/Au flower-like structures: PVD process

- *Deposition of a thin coating of gold (2-3 nm) onto pre-patterned samples*
  - *Study of their electrochemical activity*



Cyclic voltammograms (0.1 M Na2SO4, 200 mV/s, cycle 5)

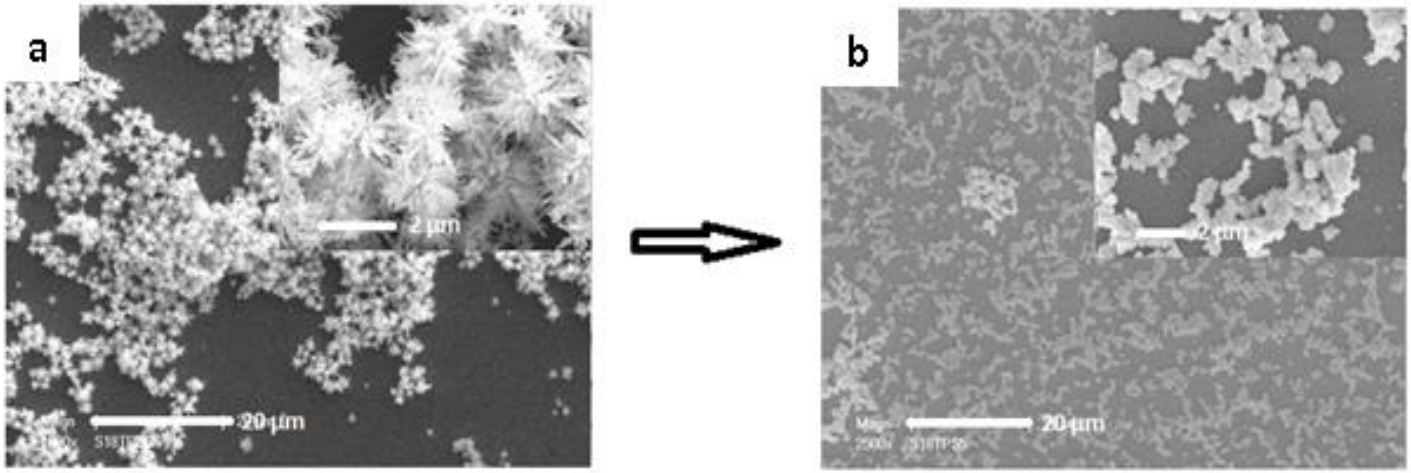
IV/ A new route: Bimetallic Ag/Au flower-like structures: The galvanic replacement

Parameters :
Ac / PS-P4VP + Seeds
$t_{immersion}$ = 1h45 + t_{HAuCl4}
$[AgNO_3]$ = 10 mM
$[HAuCl_4]$ = 2 mM
T = 30°C
without agitation
without refeeding

- *Effect of the galvanic replacement onto the pre-patterned substrates*

Cov. Rate = 31.2 %

Cov. Rate = 52.6%



SEM images of Ag/Au bimetallic nanostructures prepared with pre-patterned stainless steel substrates coated with PS-P4VP and covered with gold seeds and Ag flower-like structures

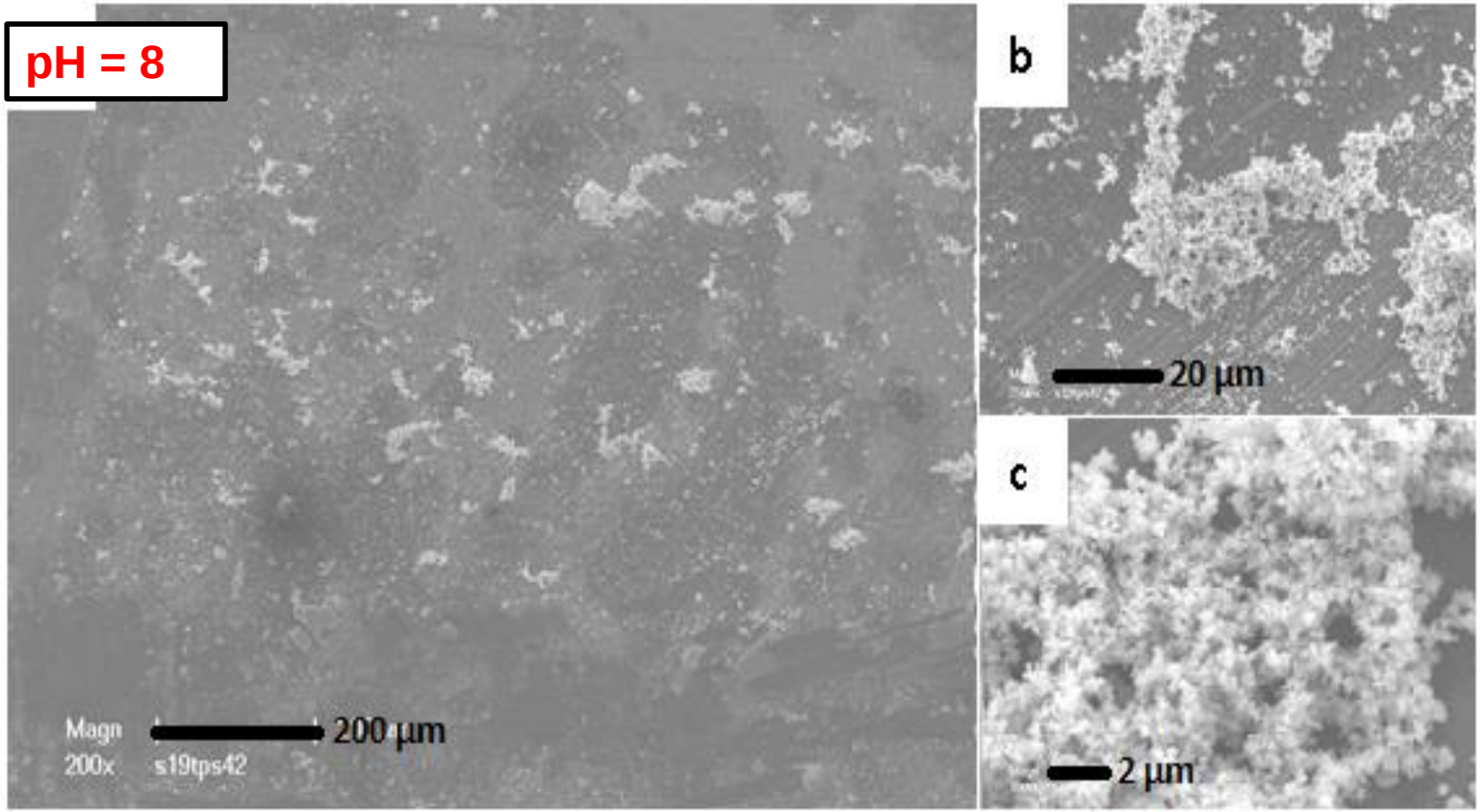
$$3Ag(s) + AuCl_4^-(aq) \rightarrow Au(s) + 3AgCl(s) + Cl^-(aq)$$

Z. Yi, S. Chen, Y. Chen, J. Luo, W. Wu, Y. Yi, Y. Tang, Thin Solid Films (2012), 520, 2701.

IV/ A new route: Bimetallic Ag/Au flower-like structures: The galvanic replacement

Parameters :
Ac / PS-P4VP + Seeds
$t_{immersion}$ = 1h45 + t_{HAuCl4}
$[AgNO_3]$ = 10 mM
$[HAuCl_4]$ = 2 mM
T = 30°C
without agitation
without refeeding

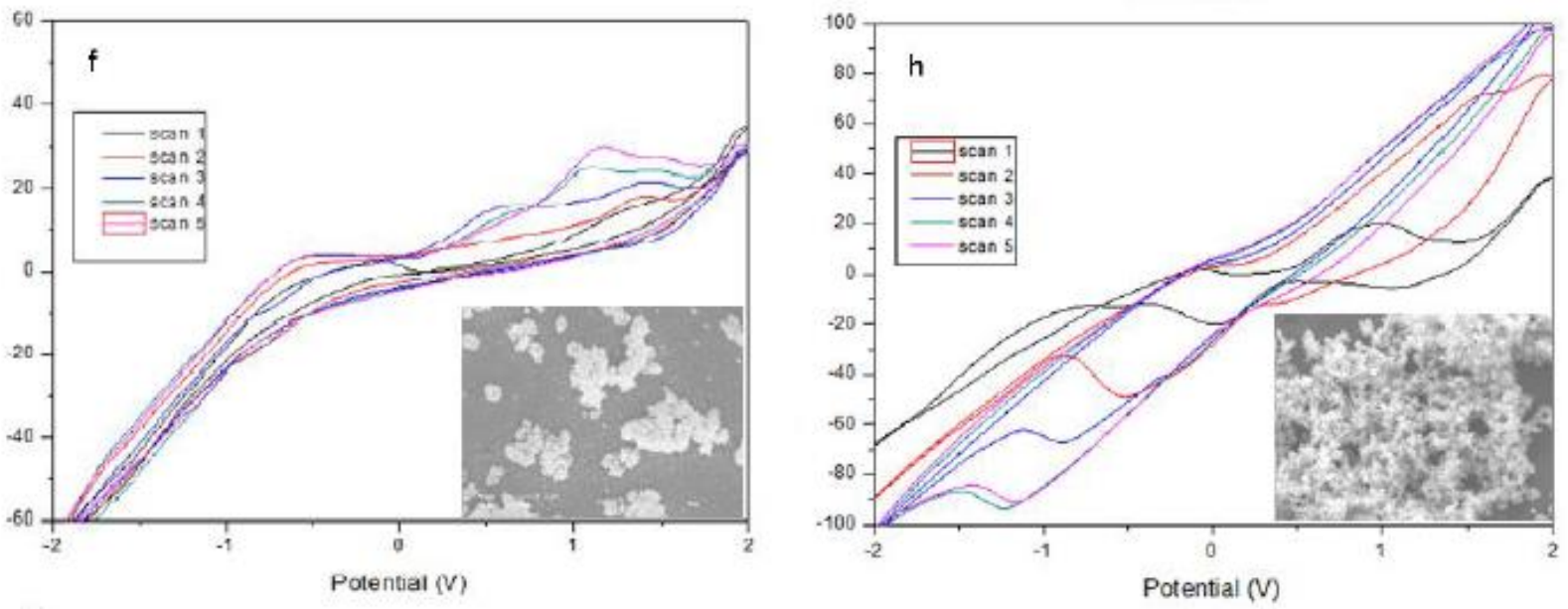
- *Effect of pH of the galvanic replacement solution onto bimetallic nanostructures*



SEM images of Ag/Au bimetallic flower-like structures prepared at pH = 8

IV/ A new route: Bimetallic Ag/Au flower-like structures: The galvanic replacement

- *Study of electrochemical activities*

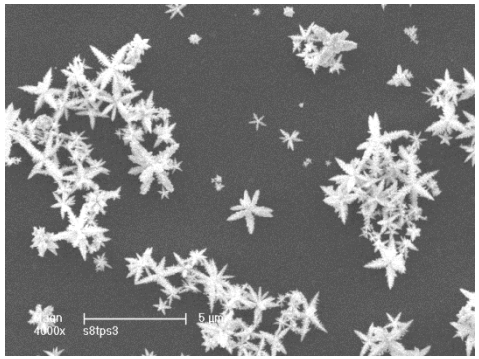
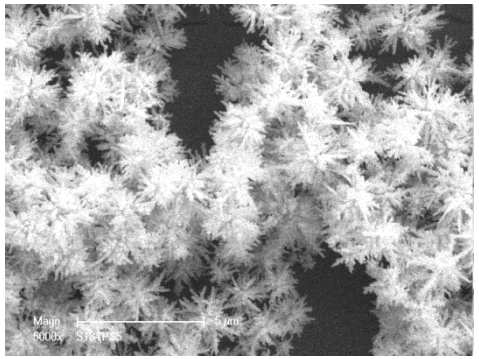
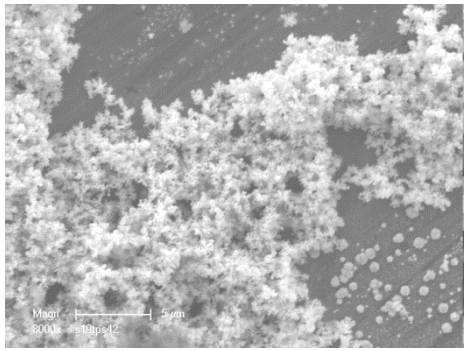


Cyclic voltammetry of bimetallic NFs at different concentrations.

Conclusion

- Optimization of flower-like growth process
  - Au (Hydroxylamine NH_2OH)
  - Ag (Ascorbic Acid)
  - Ag/Au (Ascorbic Acid + galvanic replacement)

Optimal parameters:
Stainless steel plate
$t_{immersion}$ = 1h45
[Metallic salts] = 1% wt
$pH_{structuring\ agent}$ = 4-6
T = 60/80°C
without agitation
without refeeding

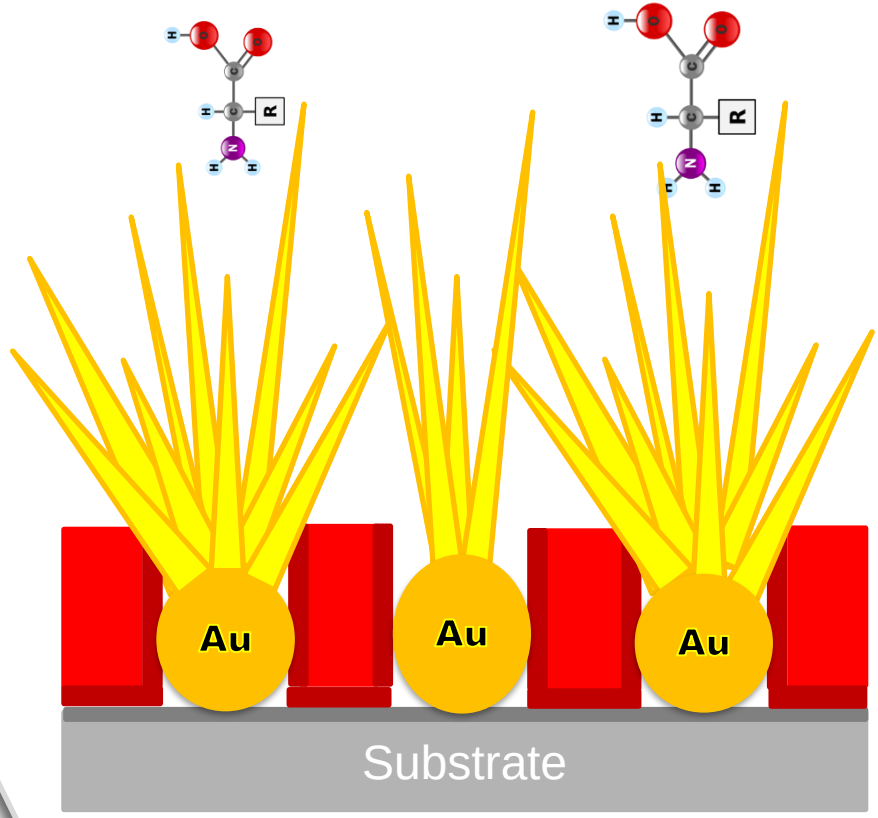
- Strong electrochemical signal for Ag flower-like structures and bimetallic flower-like structures

Perspectives

- Quantification of reaction sites, nanoflowers
  - QCM, Colorimetric method
- Understanding of growth process mechanism
- Process of SERS and electrochemical analysis
- Optimization of formation process of flower-like structures
  - Control of the NFs distribution

Objective of the project

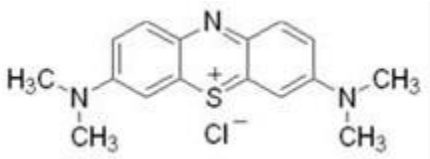
- Development of a regenerative nanosensor for detection and analysis of traces of targeted molecules
- Development of an electroactive surface made of metallic nanostructures



1) Nanostructured surface onto pre-patterned substrate with a thin film of copolymer (PS-P4VP)
2) Insertion of gold nanoparticles inside the pores of copolymer (seeds)
3) Growth of Au flower-like nanostructures onto the « seeds »
4) Selective Adsorption of targeted molecules

I/ Reminder of the conception of the active part of the sensor

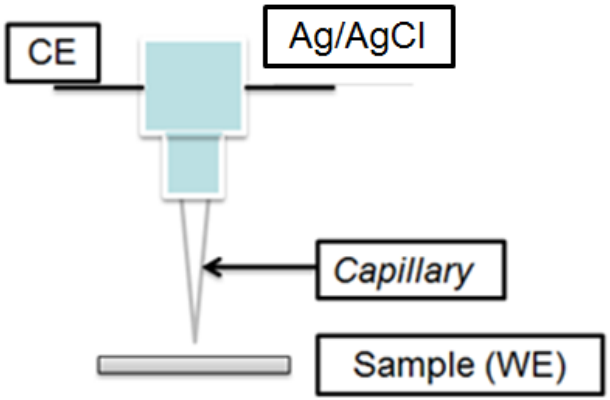
- *Optical activity:*



cm-1	Assignments
2200	R-N-C
1600	C-C and C-N-C
1400	C-C
1200	C-C and C-N-C
1000	C=N
500-600	C=C (ring)

Methylen blue (MB) : probe molecule Concentration: **10^{-5} M** for **15 minutes**
SERS Effect :
- 4 different concentrations : **10^{-5}, 10^{-7}, 10^{-9}, 10^{-11} M**

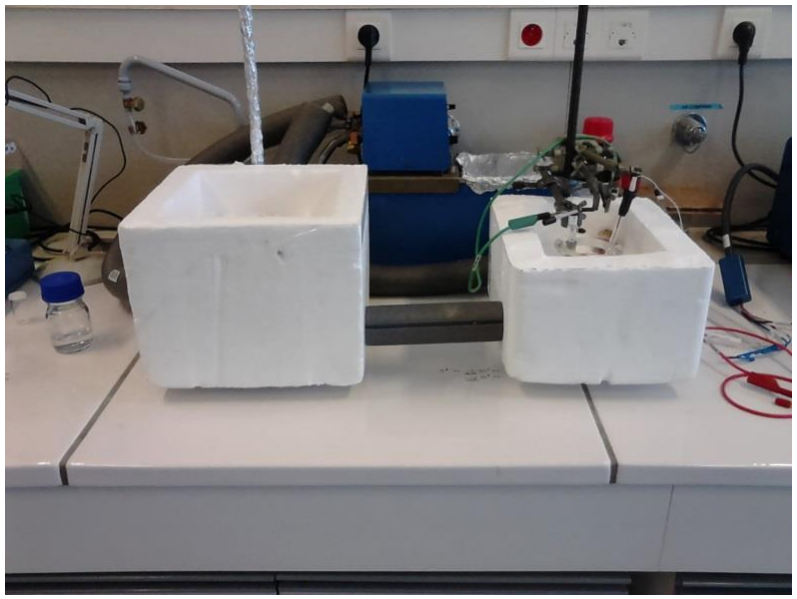
- *Electrochemical response*

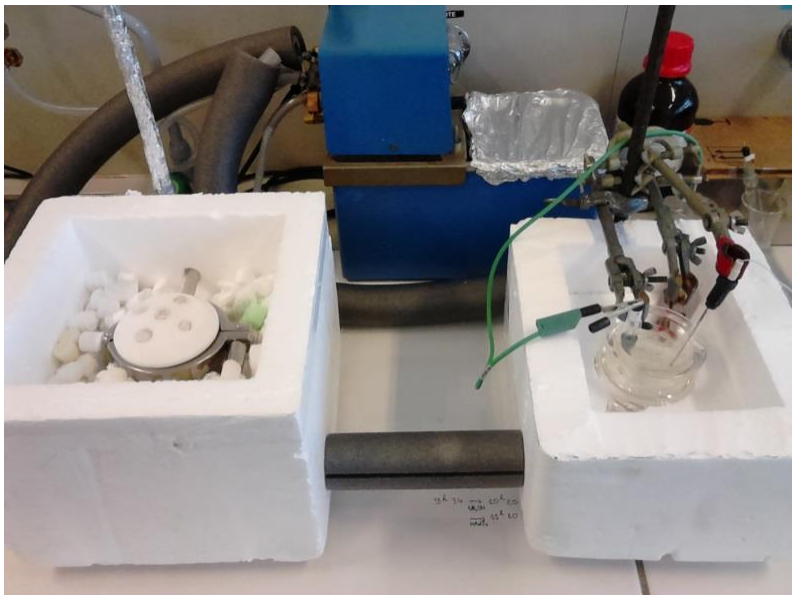


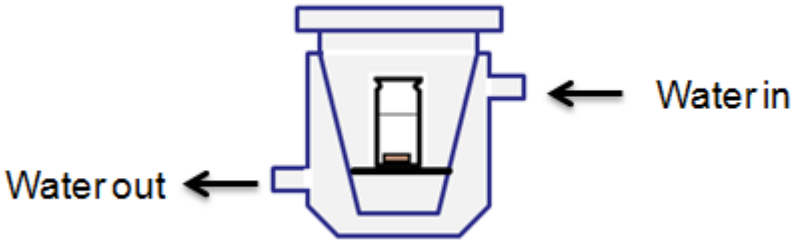
- Capillary method with microcell Na_2SO_4 (0.1 M) aqueous solution
- Cyclic voltamperometry at 200 mV/s over 5 cycles.

I/ Reminder of the conception of the active part of the sensor

- *Control of physico-chemical parameters on growth process*
  - ***Temperature***: Insulated closed double jacketed glass cell – blank with water

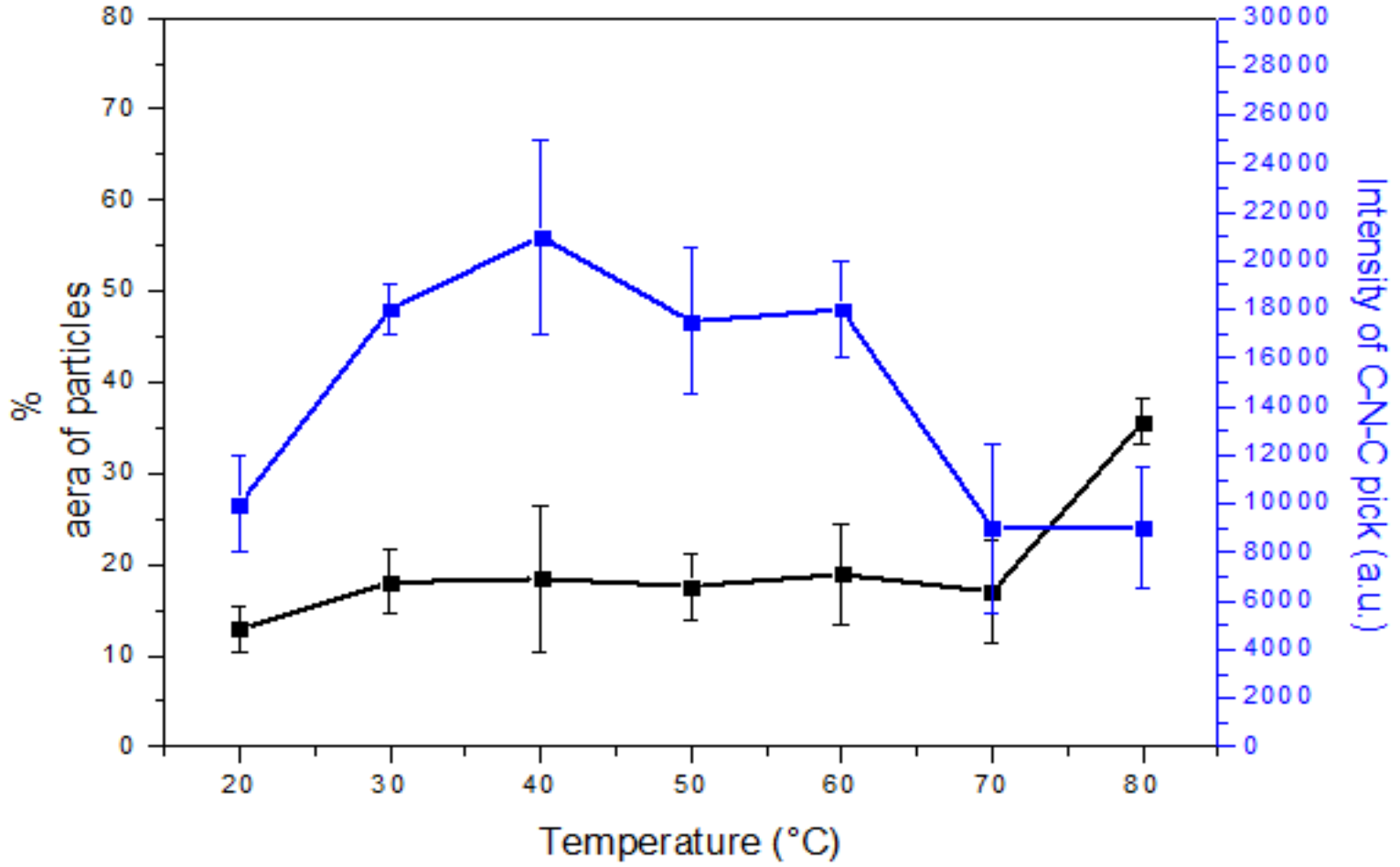






II/ Synthesis of Au flower-like structures: Optical and electrochemical properties

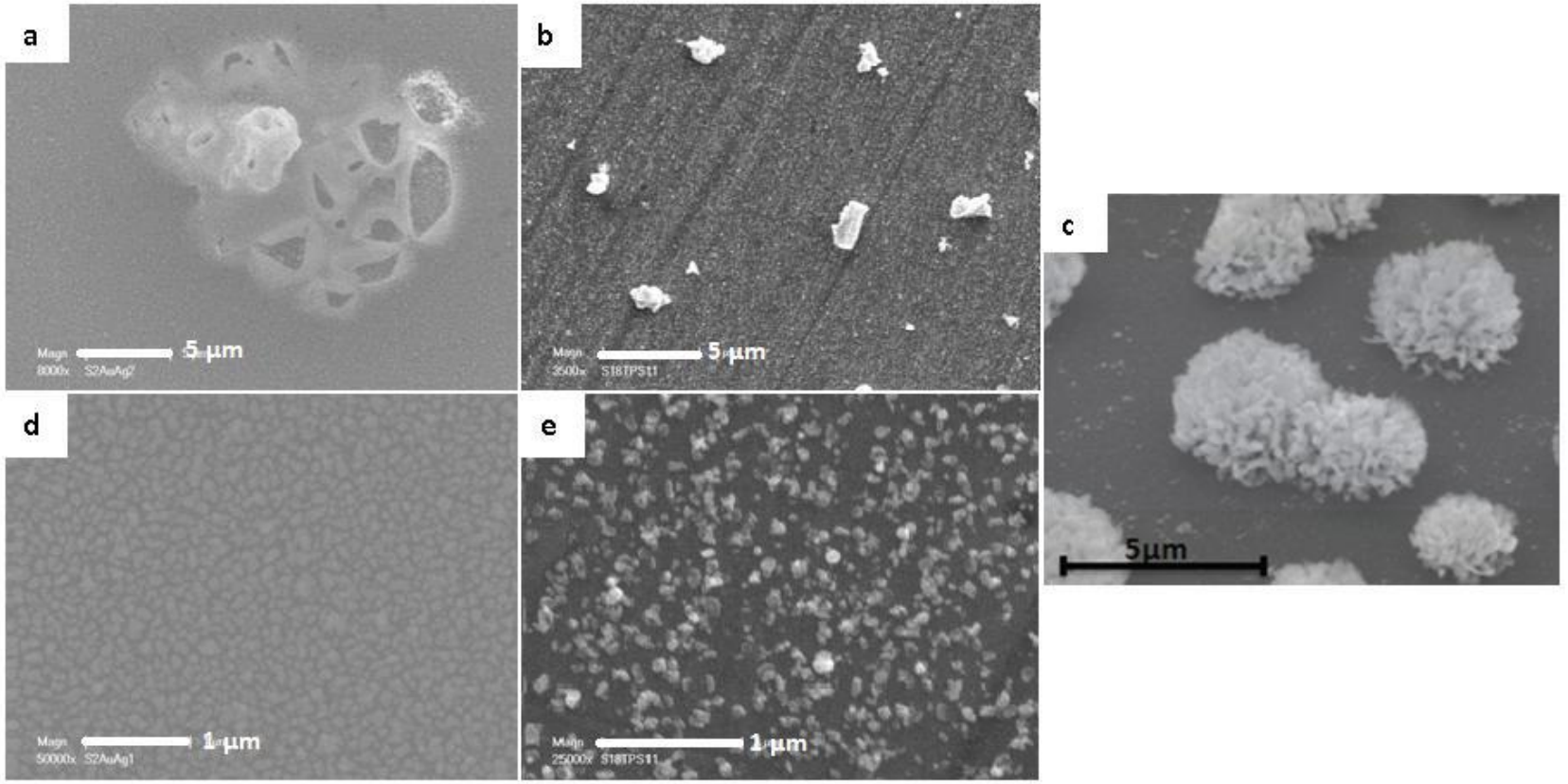
- *Effect of temperature control on **silicon wafers***



Evolution of the intensity of the C-N-C peak of the MB adsorbed on the Au flower-like structures and evolution of % area of particles vs reaction temperature.

III/ Synthesis of Ag flower-like structures: Chemical way: Citrate

- *Effect of components amounts onto structures*

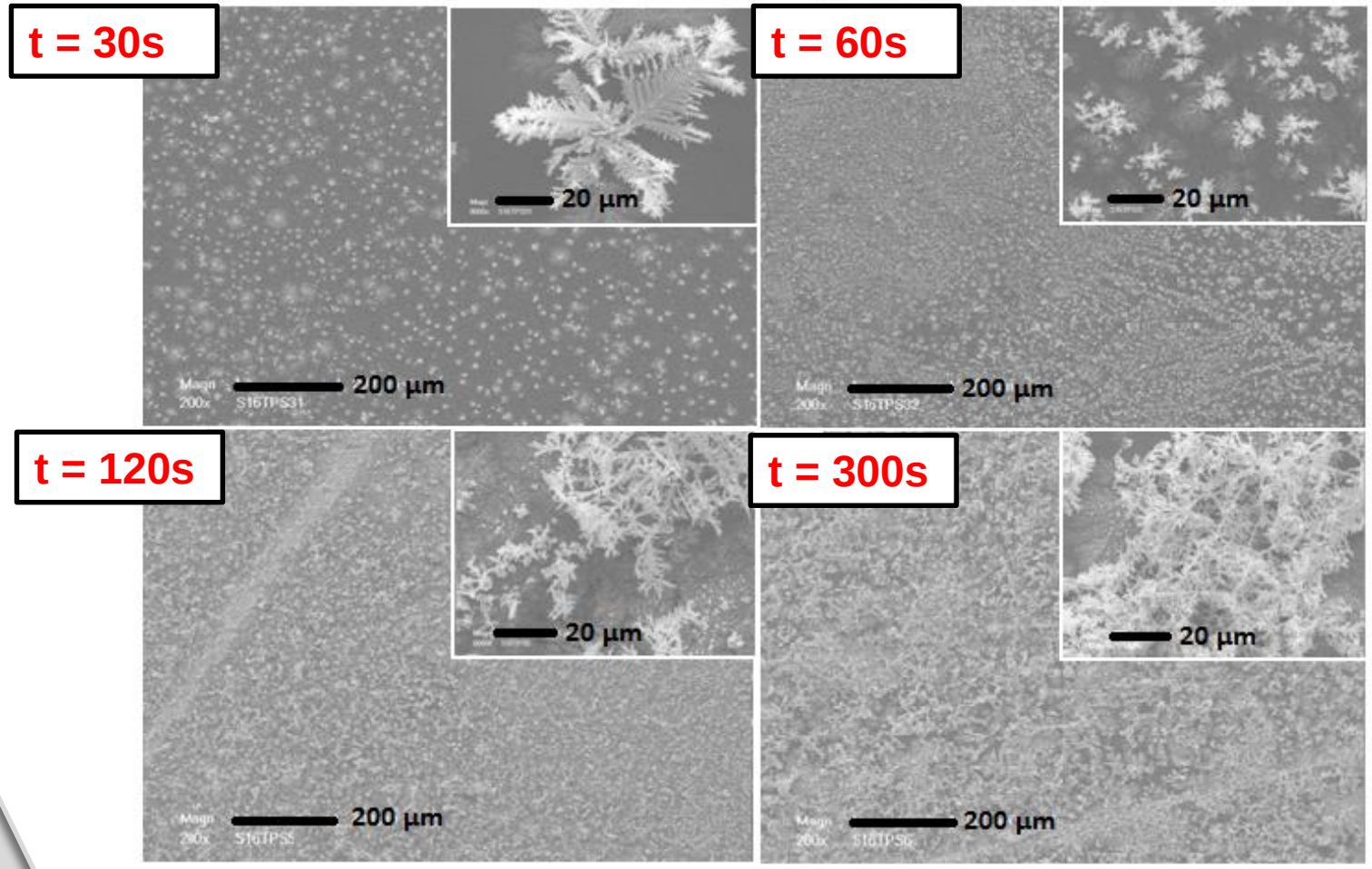


SEM images of Ag nanostructures prepared at different amounts of coponents

III/ Synthesis of Ag flower-like structures: Electrochemical way

Parameters :
Ac / PS-P4VP + Seeds
[$AgNO_3$] = 10 mM
E = -1 V
Room Temp
pH = 10
without agitation
without refeeding

- *Effect of electrolysis time on Ag dendritic structures*

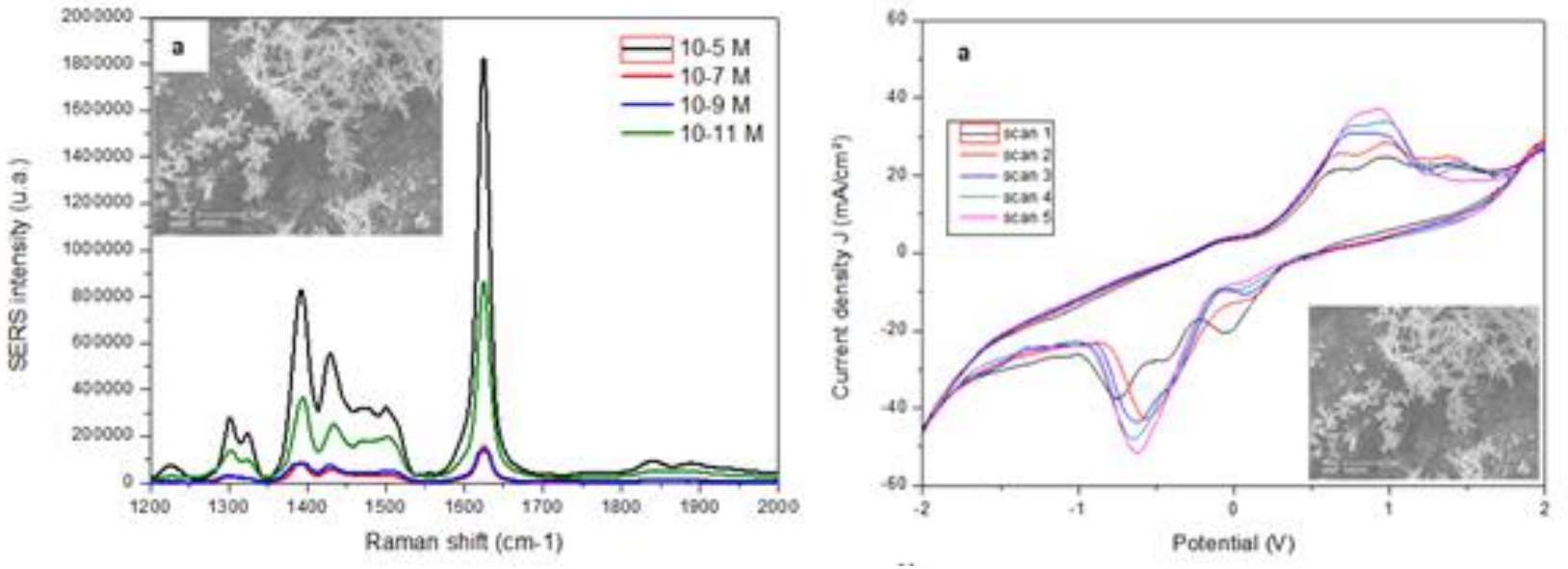


SEM images of Ag dendritic structures prepared at different electrolysis time

III/ Synthesis of Ag flower-like structures: Electrochemical way

- *Study of SERS effect and electrochemical activities*

Cov. rate = 47.1 %



SERS spectra and cyclic voltammetry of Ag dendritic structures

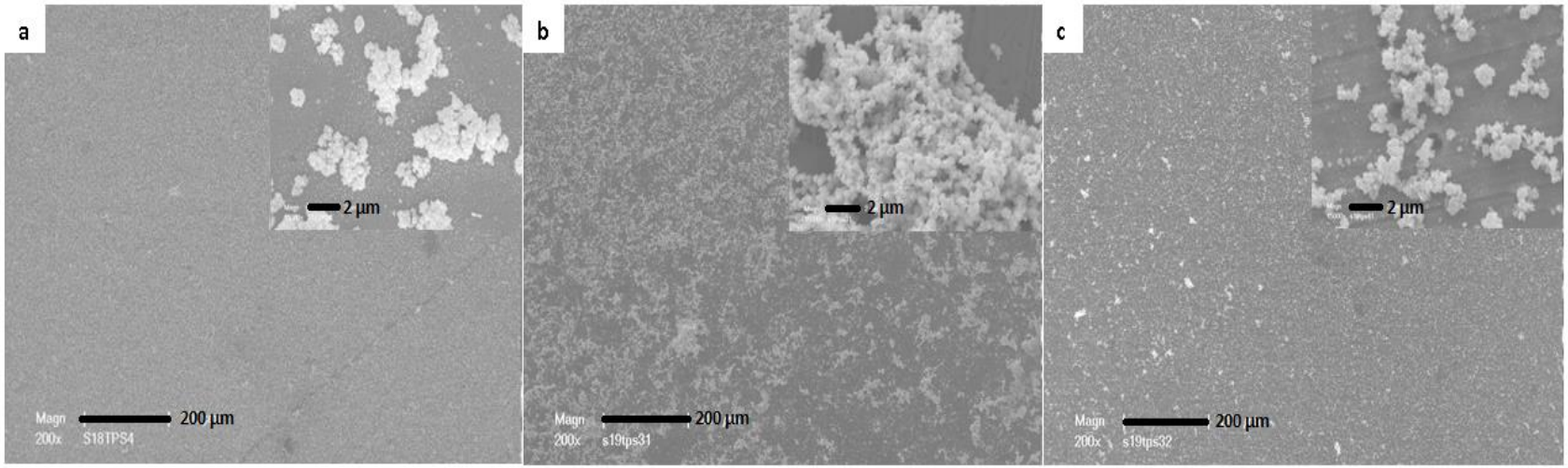
Significant SERS and El. signal for Ag nanodendrites

IV/ A new route: Bimetallic Ag/Au flower-like structures: The galvanic replacement

Parameters :
Ac / PS-P4VP + Seeds
$t_{immersion}$ = 1h45 + t_{HAuCl4}
$[AgNO_3]$ = 10 mM
$[HAuCl_4]$ = 2 mM
T = 30°C
without agitation
without refeeding

- *Effect of immersion time of samples in onto bimetallic nanostructures*

t = 1 min | **t = 2.5 min** | **t = 5 min**



SEM images of Ag/Au bimetallic nanostructures prepared at different immersion time