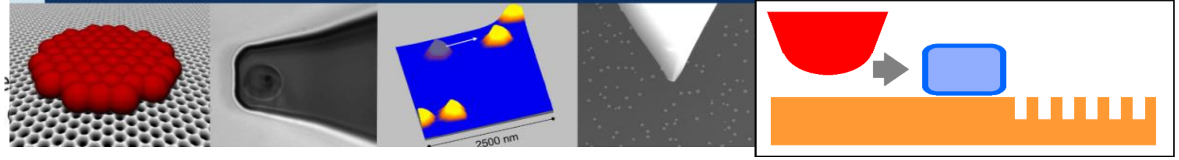
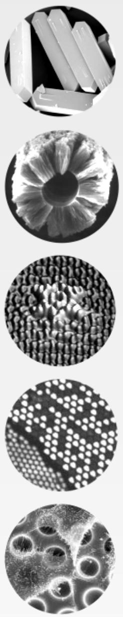




Institut de Science des Matériaux de Mulhouse

" Effect of Relative Humidity when Manipulating Au NPs on Flat Substrates using Dynamic AFM"

Samer DARWICH[1], Karine MOUGIN[1], Hendrick HOELSHER[2], Enrico GNECCO[3], and Hamidou HAIDARA[1]

[1] Institut de sciences des matériaux de Mulhouse, 15 rue Jean Starcky, 6 8057 Mulhouse, France.
[2] Institut für Mikrostrukturtechnik, Universität Karlsruhe (TH), Hermann-von-Helmholtz-Platz 1 76344 Eggenstein-Leopoldshafen, Germany.
IMDEA Nanoscience, Avda. Fco. Tomás y Valiente, 7, Facultad de Ciencias, Módulo C-IX 3ª planta Ciudad Universitaria de Cantoblanco, 28049 Madrid, spain

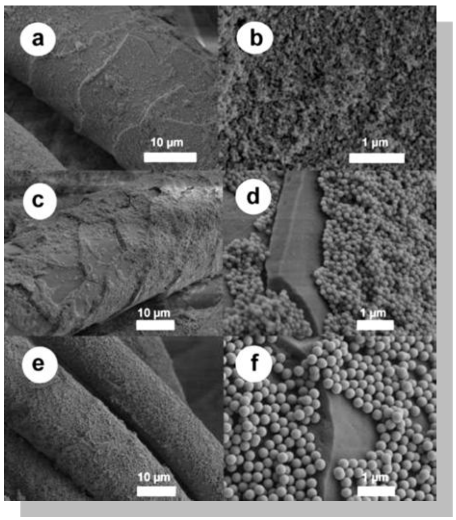
Joint ICTP-FANAS Conference on trends in Nanotribology

Trieste – Italy, 12-16 September 2011

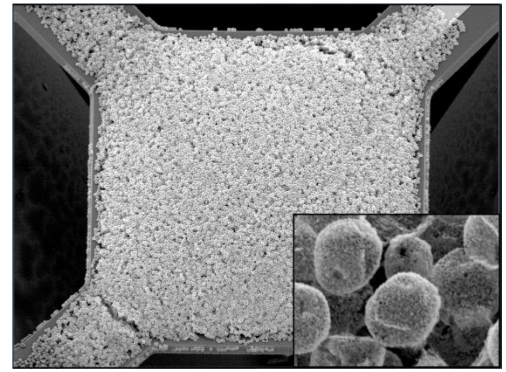
European Science Foundation
SETTING SCIENCE AGENDAS FOR EUROPE

Nanoparticules deposited on materials surface…

… self-assembled NPs …



« Fabricating Superhydrophilic Wool Fabrics »
Dong Chen, Longfei Tan, Huiyu Liu, Junyan Hu, Yi Li and Fangqiong Tang
Langmuir, vol. 26, **(2010)**, 4675–4679



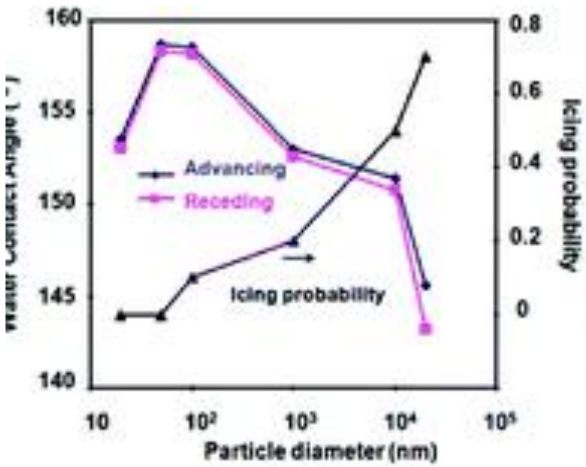
« Microsensors in Dynamic Backgrounds: Toward Real-Time Breath Monitoring »
K.D. Benkstein, B. Raman, C.B. Montgomery, C.J. Martinez and S. Semancik
Sensors Journal IEEE, vol. 10, **(2010)**, 137-144

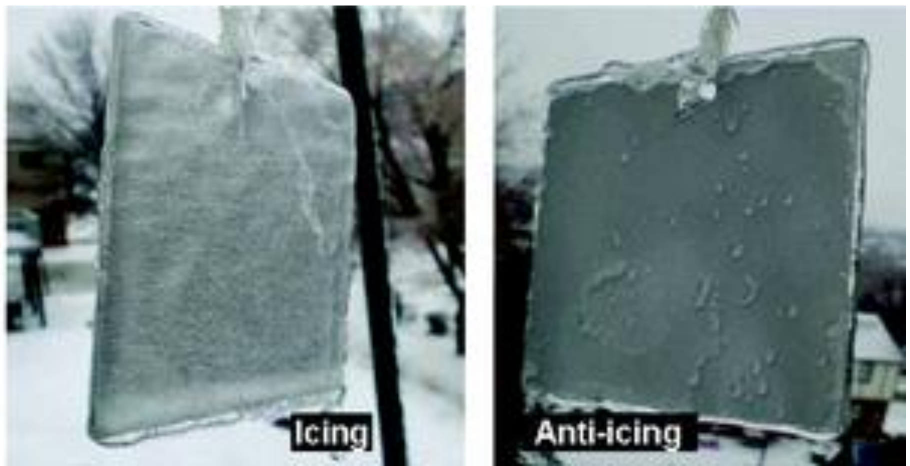
… or isolated …

… to create novel physical or mechanical properties

or improved old ones…

To fabricate highly hydrophobic coatings



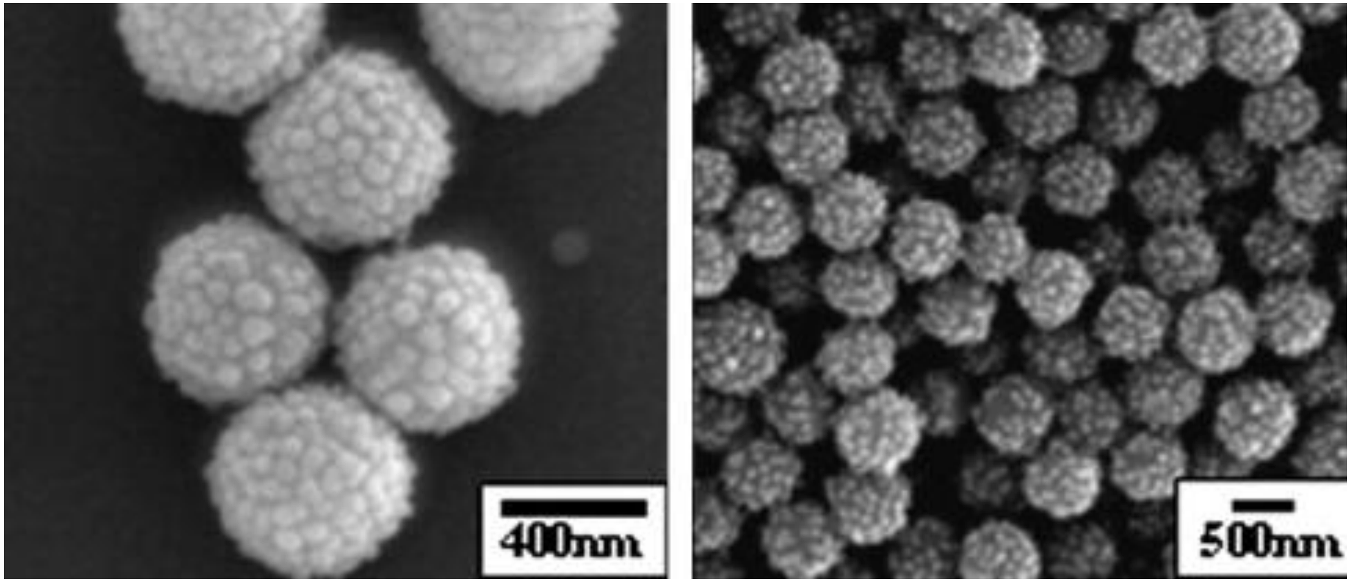


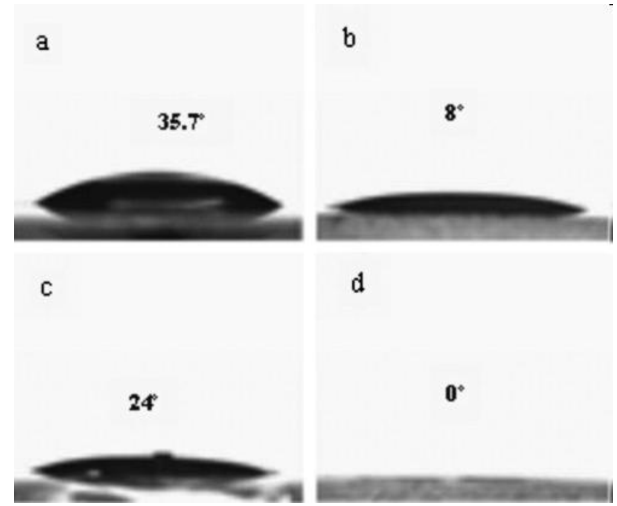
Anti-Icing Superhydrophobic Coatings

§ Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521

Langmuir, 2009, 25 (21), pp 12444–12448

To fabricate superhydrophilic coatings





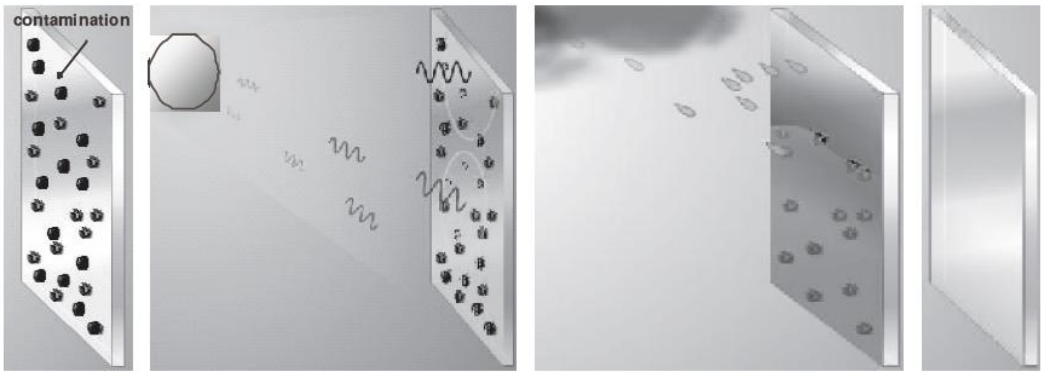
Hierarchically structured superhydrophilic coatings fabricated by self-assembling raspberry-like silica nanospheres

Xiangmei Liu and Junhui He

Journal of Colloid and Interface Science 314,(1), pp341-345, **2007**

Ti O2 nanoparticles

➡ For self- cleaning functional and environmentally friendly coatings



Photocatalyse: décomposition de la contamination

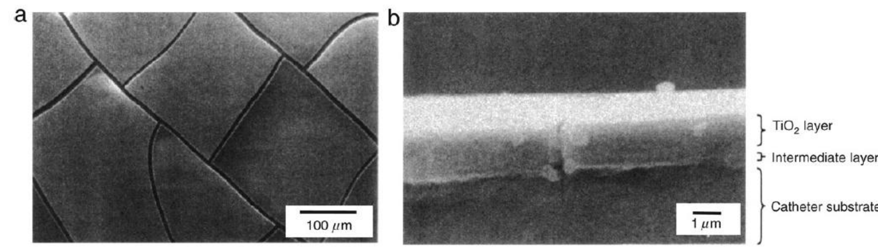
Super-hydrophilie photo-induite: rinçage de la contamination résiduelle

Ti O2 nanoparticles

- anti-fogging, Air conditionning,…

http://www.toto.co.jp

- For self- sterilisable coatings

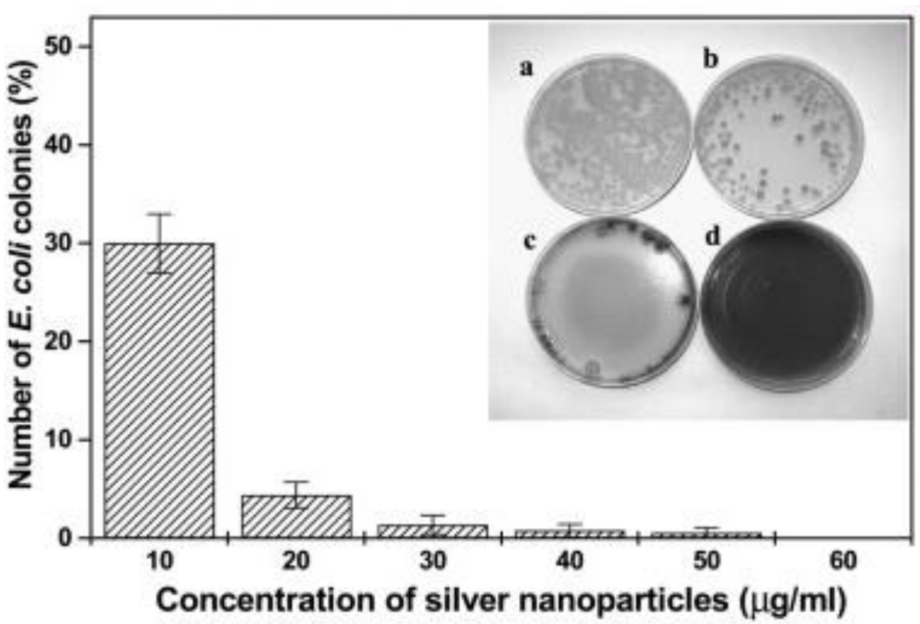


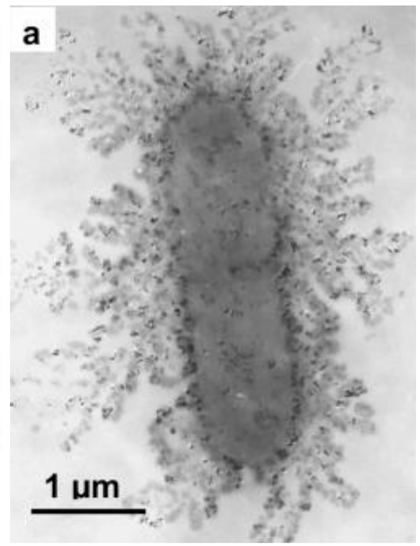
- For self-depolluting systems

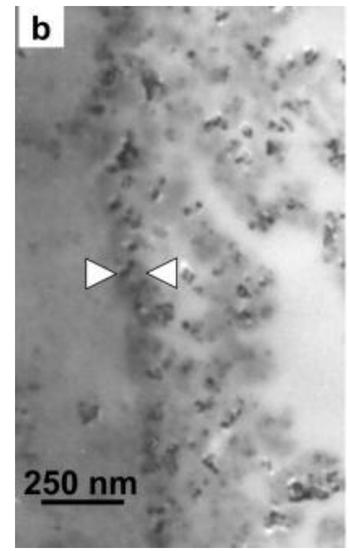
Fig. 6.7. Usage of TiO_2-based photocatalytic material on roadway surfaces to convert nitrogen oxides (NO_x) to nitrate: (left) application of the coating; and (right) finished roadway, with the coated surface showing a lighter color (courtesy of Fujita Road Construction Co., Ltd.).

TiO2 photocatalysis and related surface phenomena
Akira Fujishima, Xintong Zhang and Donald A. Tryk
Surface Science Reports, 63 (12), pp 515-582, **2008**

Ag nanoparticules d'Ag for antimicrobial agent coatings

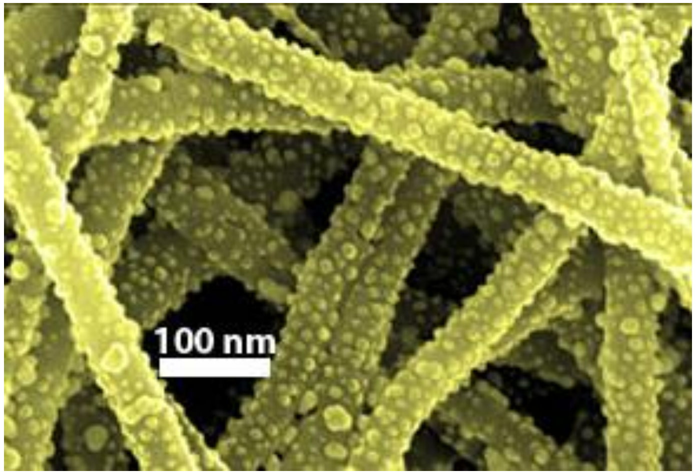






Silver nanoparticles as antimicrobial agent:
a case study on *E. coli* as a model for Gram-negative bacteria
Ivan Sondiand Branka Salopek-Sondi
Journal of Colloid and Interface Science, 275 (1), pp177-182, **2004**

Ag nanoparticules for nanotextile coatings



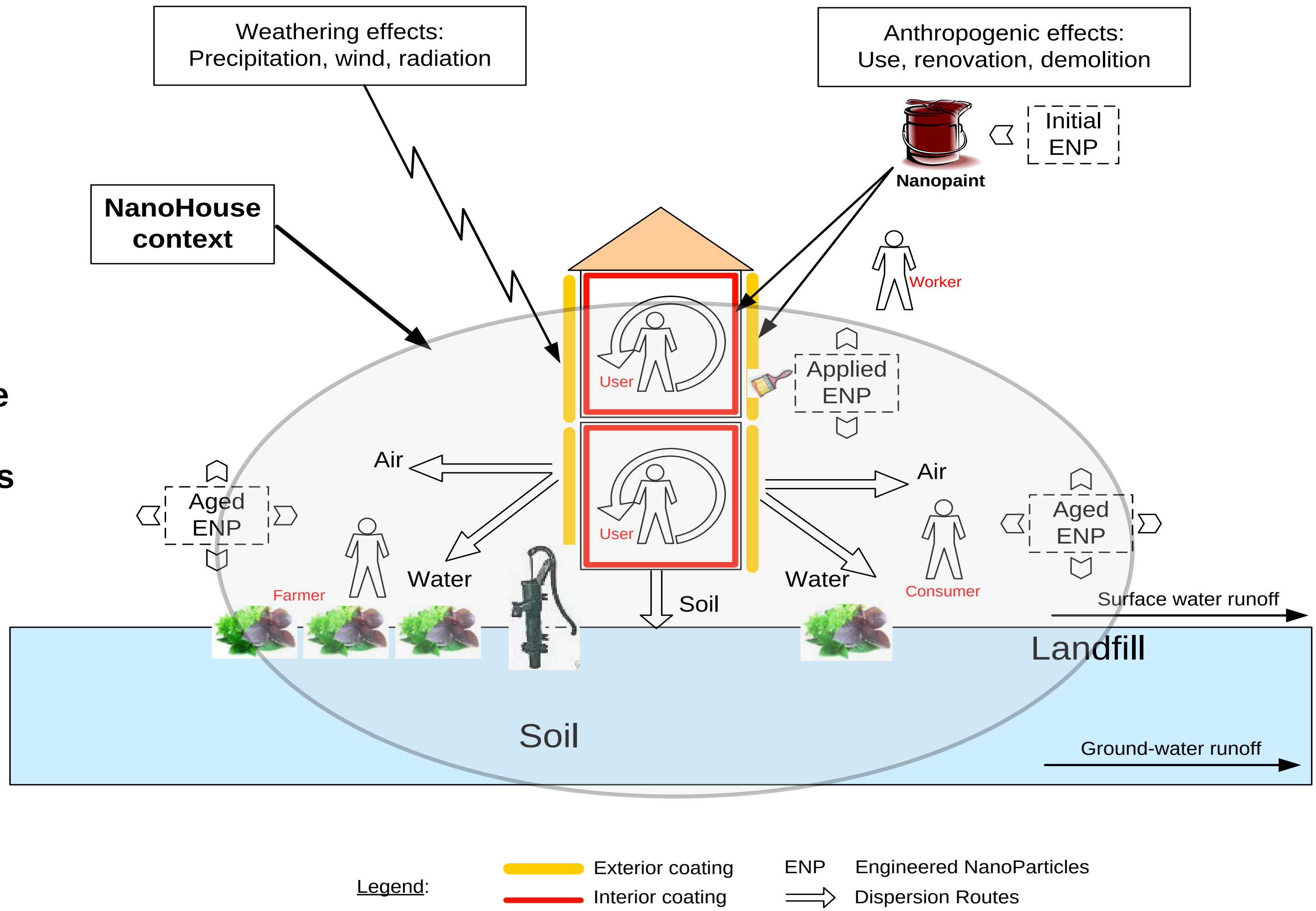
http://nanotextiles.human.cornell.edu/research.htm

Preparation and characterization of polypropylene/silver nanocomposite fibers
Sang Young Yeo, Sung Hoon Jeong
Polymer International, 52 (7), pp 1053–1057, 2003

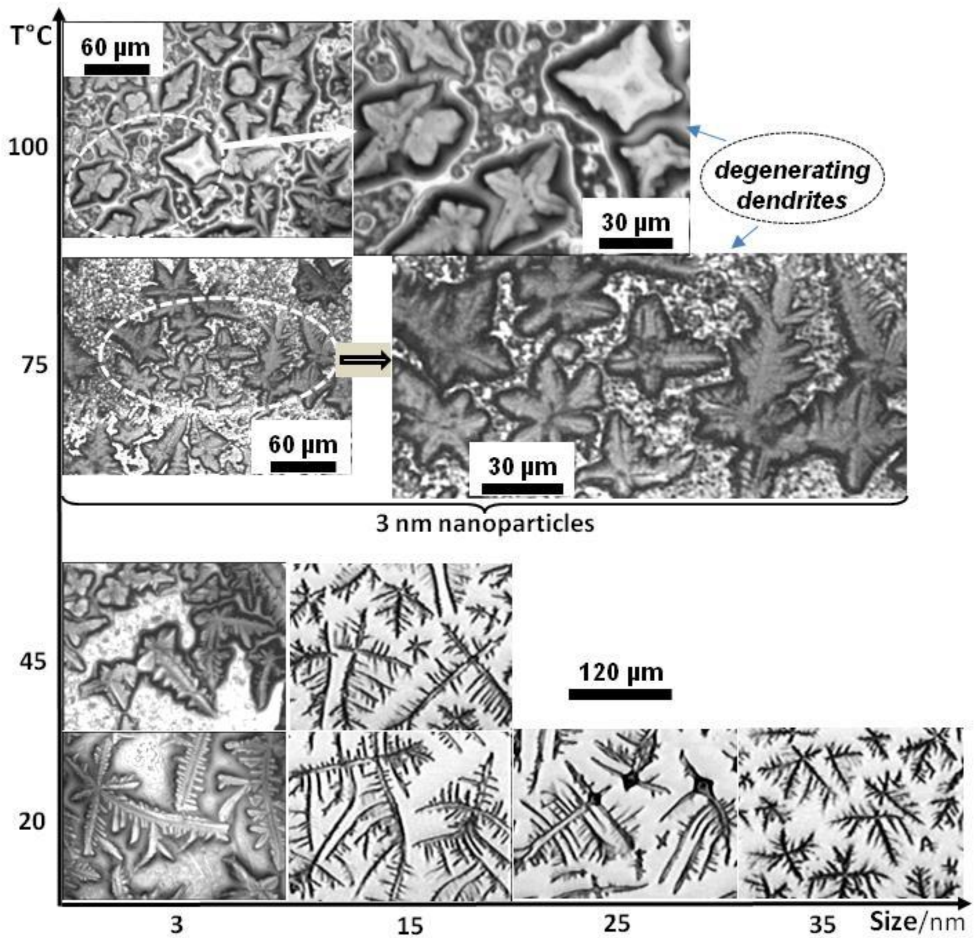
Antibacterial Effect of Silver Nanoparticles Produced by Fungal Process on Textile Fabrics and Their Effluent Treatment
Durán, Nelson; Marcato, Priscyla D.; De Souza, Gabriel I.H.; Alves, Oswaldo L.; Esposito, ElisaJournal of Biomedical Nanotechnology, 3 (2), pp. 203-208, 2007

air purification, thermal insulation, self cleaning

nano silver and
nano titanium dioxide
contained in indoor
and outdoor coatings
and paints



Stability and ageing of NPs based materials?



Environmental parameters affecting NPs arrangement:

-Temperature
-Humidity

The organization of NPs has a direct impact on their interfacial properties

Final drying patterns of nanocolloids suspensions of varying size on SiO_2, at different drying temperatures. For (15 nm; T > 45°C) and (25, 35 nm; T > 20°C), o nly featureless particle deposits are formed in the final drying spot; the occurrence of the structures is zero for these conditions.

Stability and ageing of NPs based materials?

Mechanism underlying the destabilization of the assembly of NPs

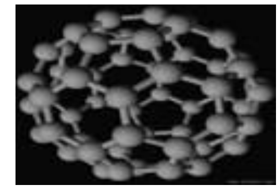
- Main forces driving the disassembly of NPs in complex structures

-Which kind of NPs shall we use to create new NPs based materials (nature, size, shape, Nps coating…..) ?

Investigation at nanoscale by AFM..

Strategies of Manipulation

- Scanning Tunneling Microscopy



R. Lüthi et al., "*Sled-type motion on the nanometer scale: Determination of dissipation and cohesive energy of C_{60}*", Science 266 (1994) 1979

M.T. Cuberes, R.R. Schlitter, and J.K. Gimzewski, "*Room-Temperature repositioning of individual C60 molecules at Cu steps: Operation of a molecular counting device*" Appl. Phys. Lett. 69 (1996) 3016.

-Surface Force Microscope in dynamic Mode

C. Ritter, Langmuir ***2002, 18, 7798-7803***

Latex

- Atomic Force Microscopy

- Contact Mode or NC mode

C. Ritter, et al, PHYSICAL REVIEW B 71, 085405 (2005)

Dirk Dietzel, JOURNAL OF APPLIED PHYSICS 102, 084306 (2007).

: a push one and an "tip-on-top" manipulation

Sb

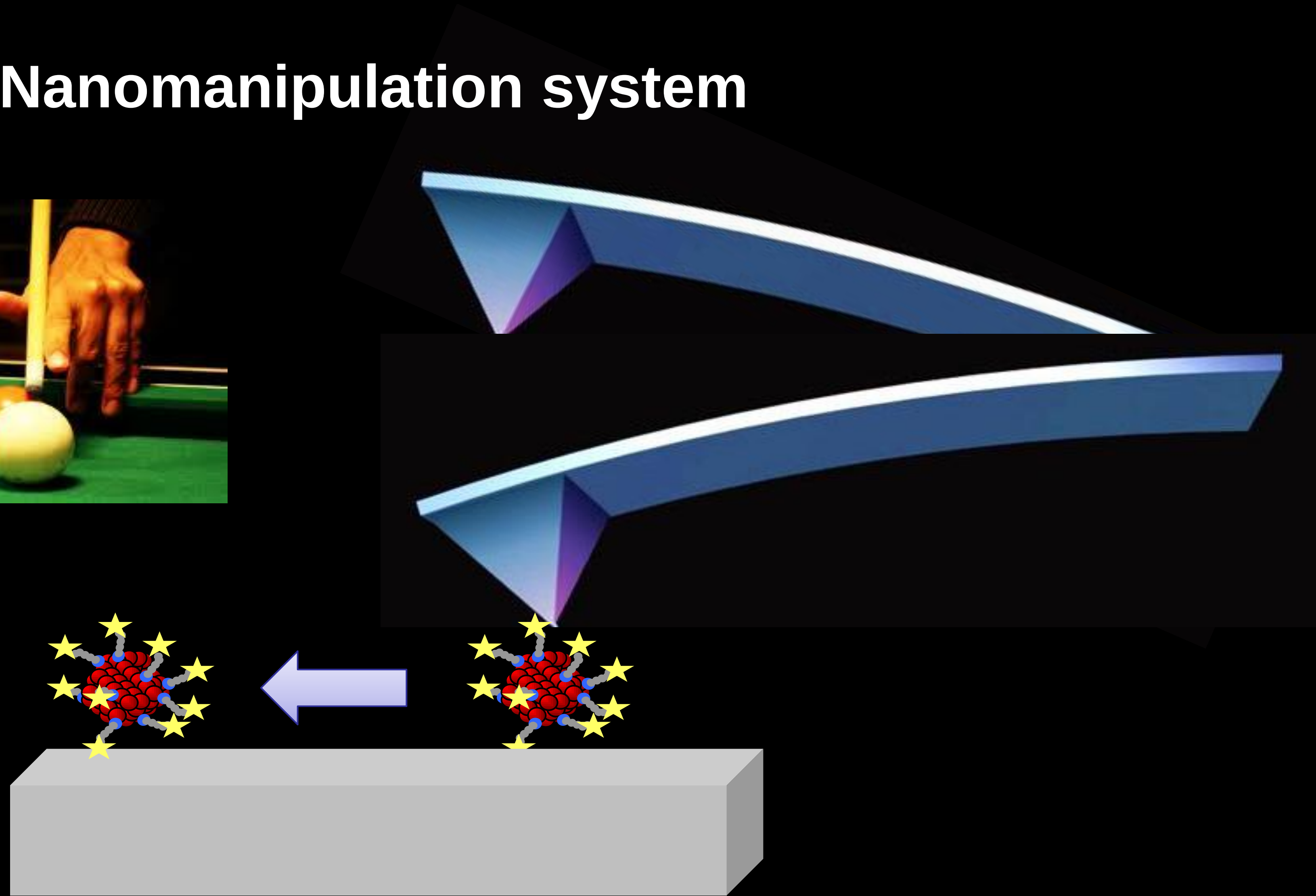
-Tapping Mode

- K. Mougin et al Langmuir 2008, 24, 1577.

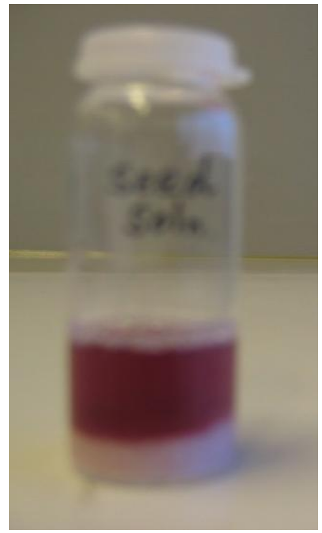
--A. Rao et al. Nanotechnology **20 (2009) 115706**

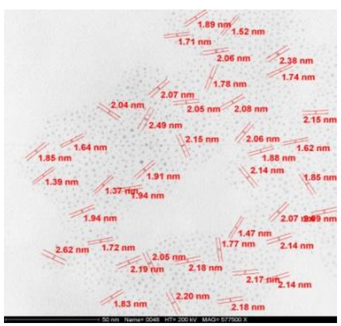
Au

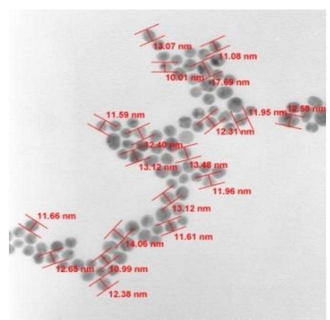
Nanomanipulation system

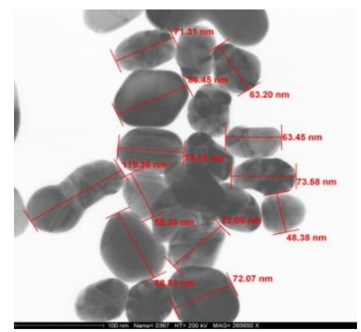


Spherical nanocolloidal gold particles







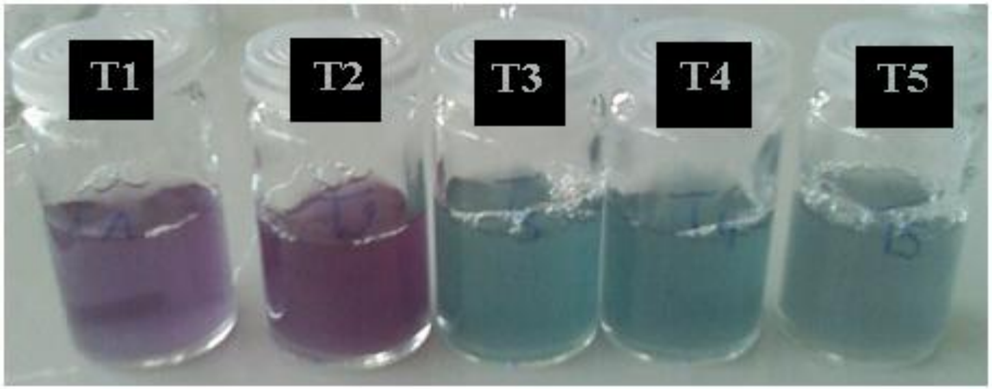


Elghanian, R.; Storhoff, J.J.; Mucic, R.C.; Letsinger, R.L.; Mirkin, C.A. "Selective colorimetric detection of polynucleotides based on the distance-dependent optical properties of gold nanoparticles" *Science* ***1997, 277,1078.***

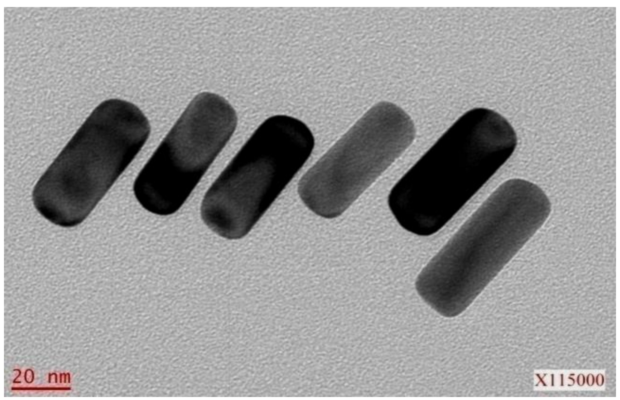
Marie-Christine,D.; Didier,A. "Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology" *Chemical reviews* ***2004, 104, 293*** and references therein

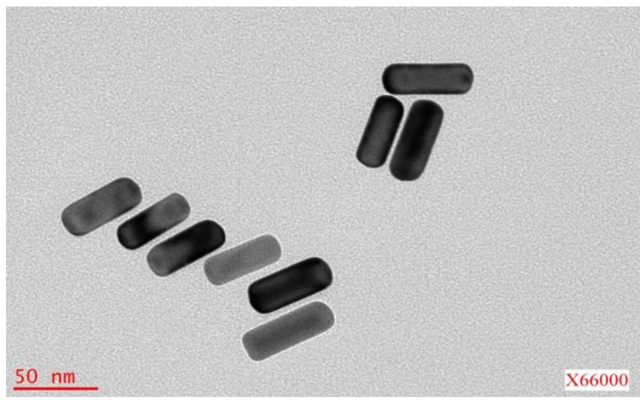
Cubooctahedral Nanocolloidal gold particles

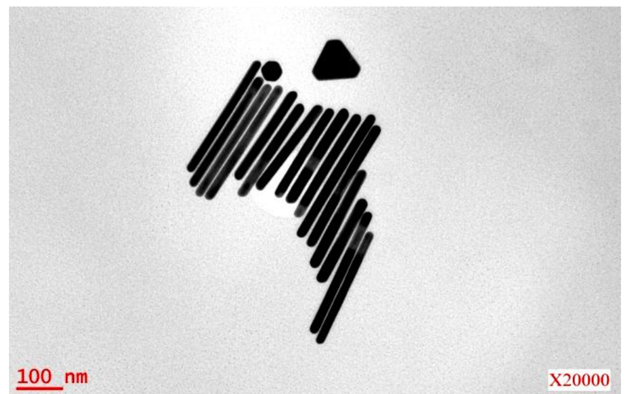
Increase of L/D Ratio



Brown, K. R. *J. Chem. Mater. 2000, 12, 306.*
Busbee, B.D.; *Advanced Materials 2003, 15, 414.*
Nikoobakht, B; El-Sayed, M. A. *Chem.Mater. 2003, 15,* 1957.



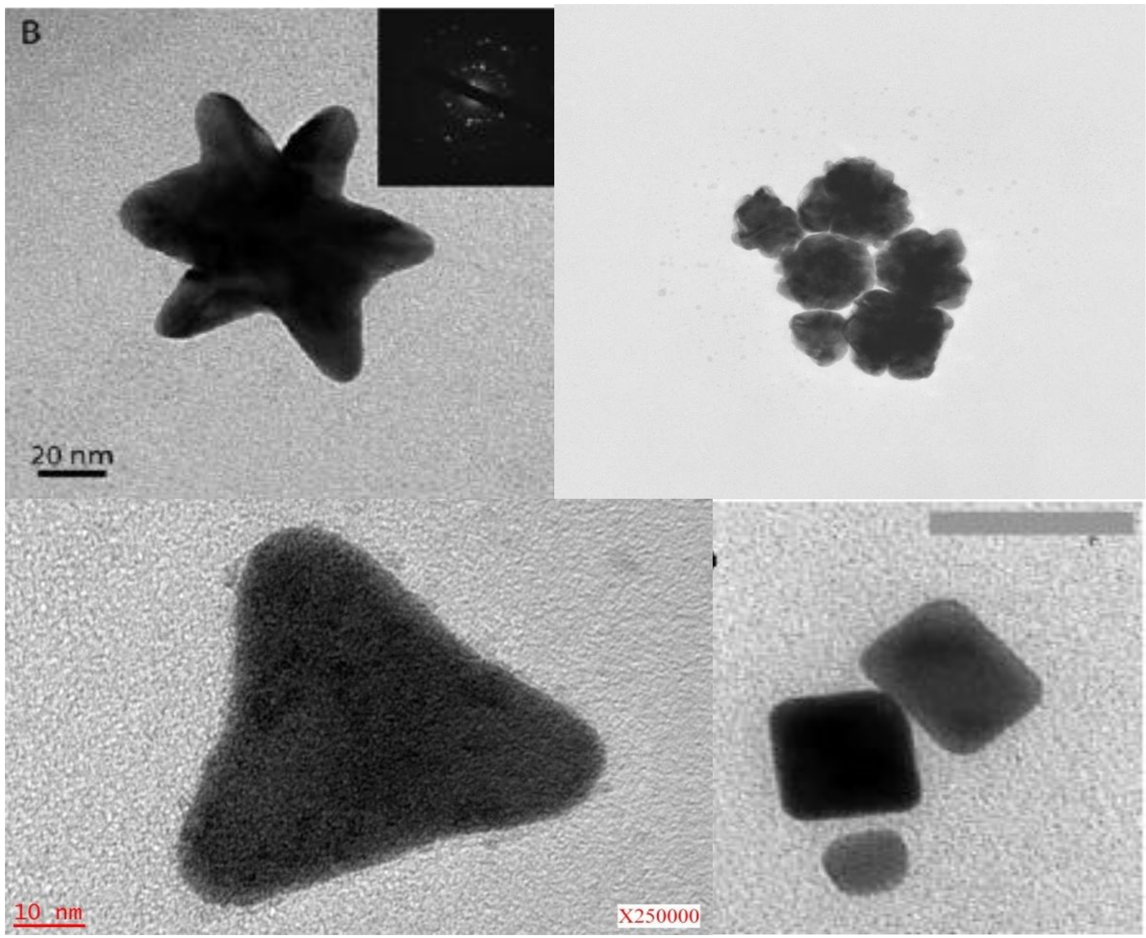




Other Nanocolloidal gold particles

Nanostar

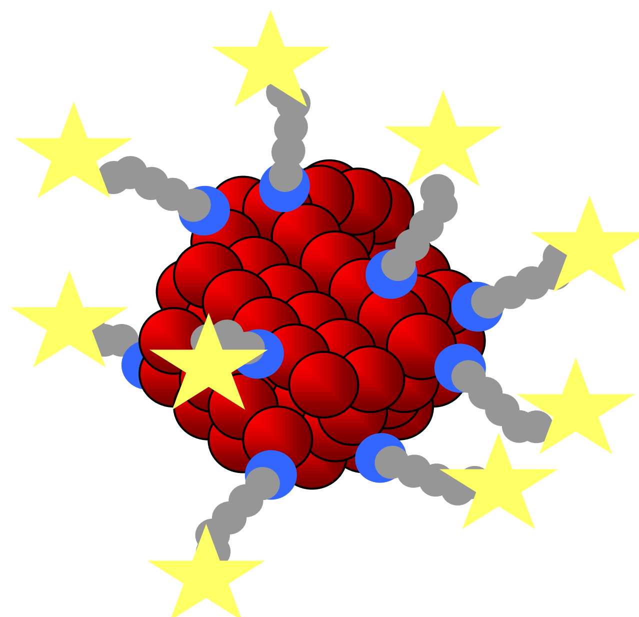
Nanoflowers



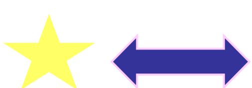
Nanotriangle

Nanocubes

Functionalization of gold nanoparticles



Terminal functionality



-CH_3
-CF_3
-OH
-NH_2
-COOH…..

Assembly of nanoparticles

1-D, 2D or 3 Dimension

- **Drying –mediated assembly or evaporation –induced assembly**

Simplest method of assembling NPs on a surface

- **Chemically assisted assembly**

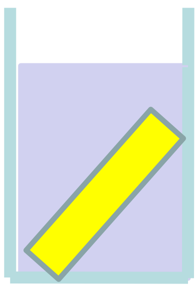
Powerful approach to create highly ordered specific nanoparticles patterns

- **Topographycally assisted assembly**

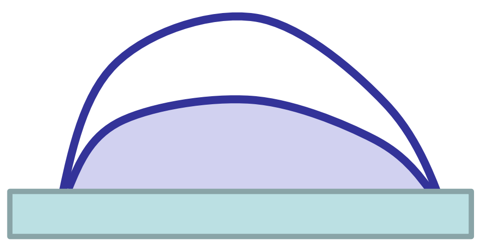
- **Mechanically assisted assembly - manipulation**

Drying-mediated Assembly of gold nanoparticles

1. Immersion of Samples into the soluton



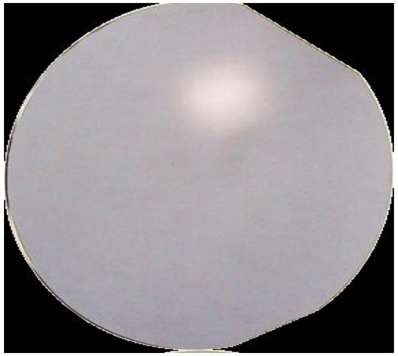
2. Drying of drop



@ different temperatures

Ph-d thesis Kyumin Lee –EPFL Kulik 2008

3. Spray coating



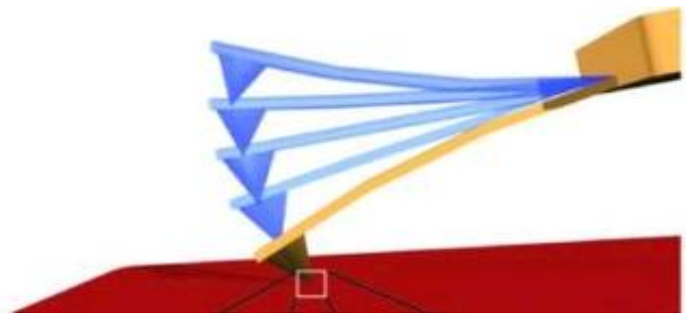
Multimode: VEECO

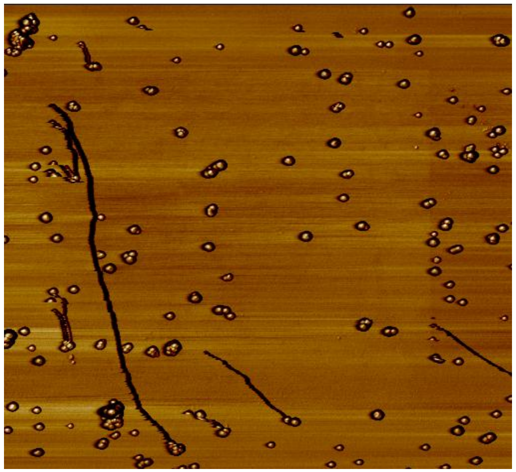
Nanoscope V

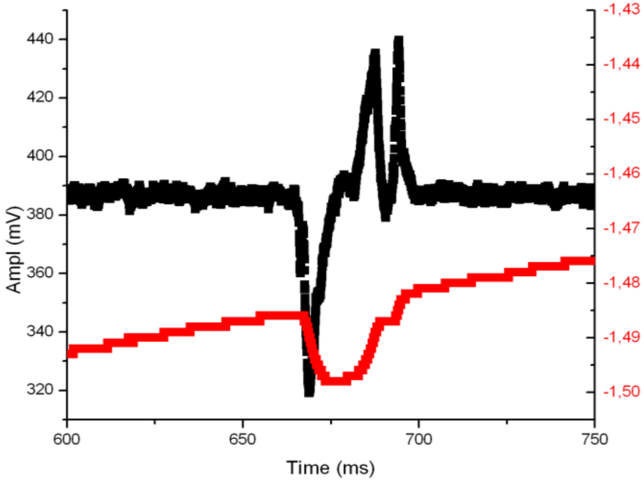
the power dissipation

$$P_{dis} = k\pi f_0 \left(A_d A \sin\varphi - \frac{A^2}{Q} \right)$$

oscillation amplitude
frequency
phase shift
drive amplitude

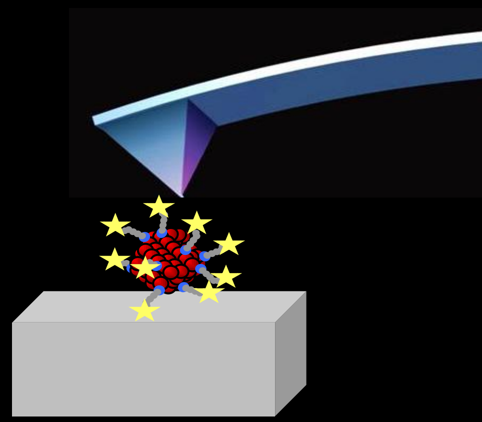






Manipulation parameters

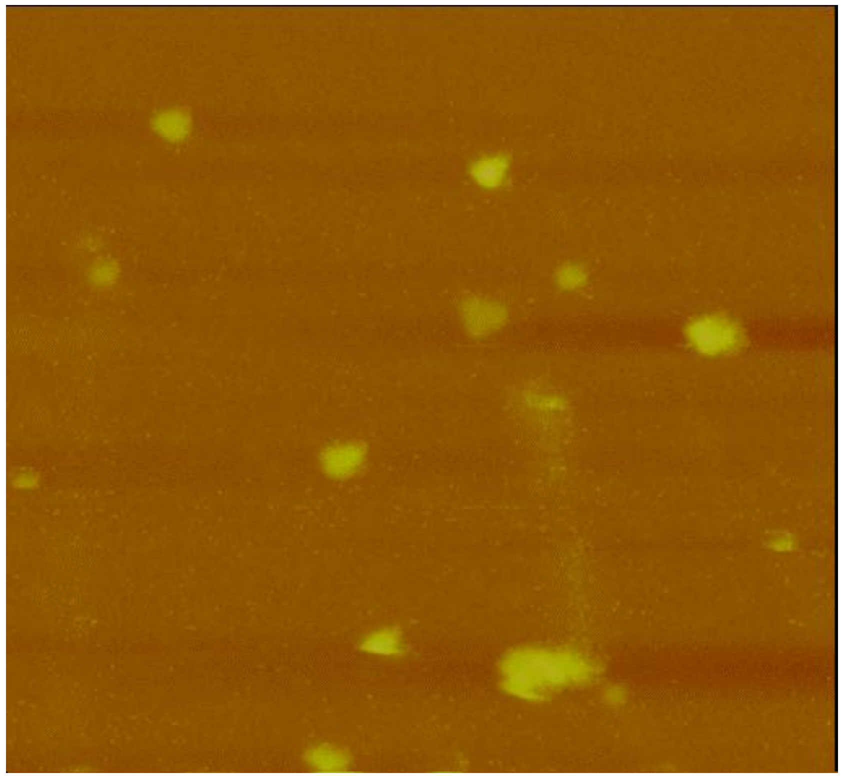
1. Structural NPs properties (Size, shape, nature)
2. Chemical coating : Nps & substrate
3. Nps distribution



4. Environment Humidity, temperature, Vacuum
5. Substrate Topography
6. Tip scan Velocity

Manipulation of gold nanoparticles by AFM in Tapping Mode

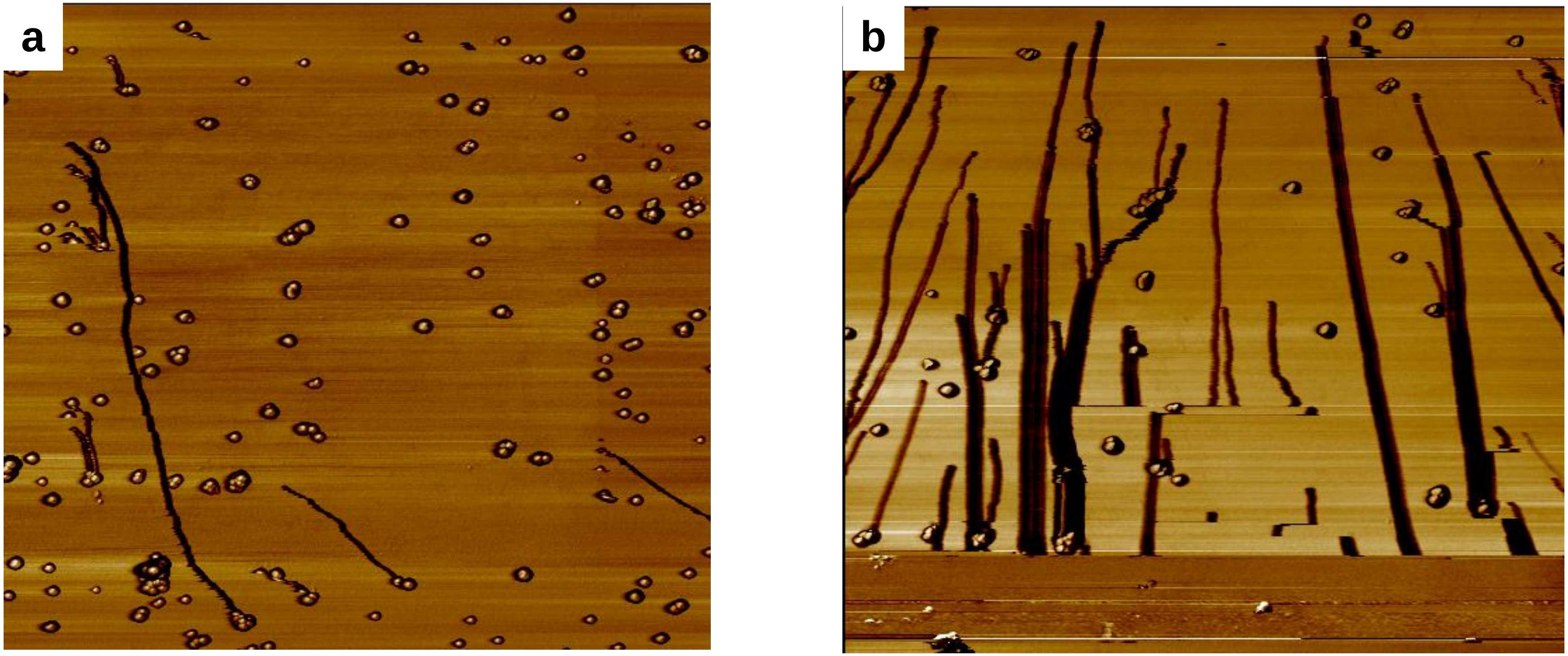
Height Signal



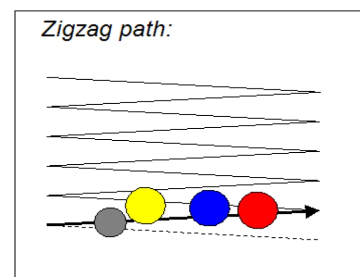
slow scan direction

Threshold energy to manipulate a particle? Sliding or rolling?

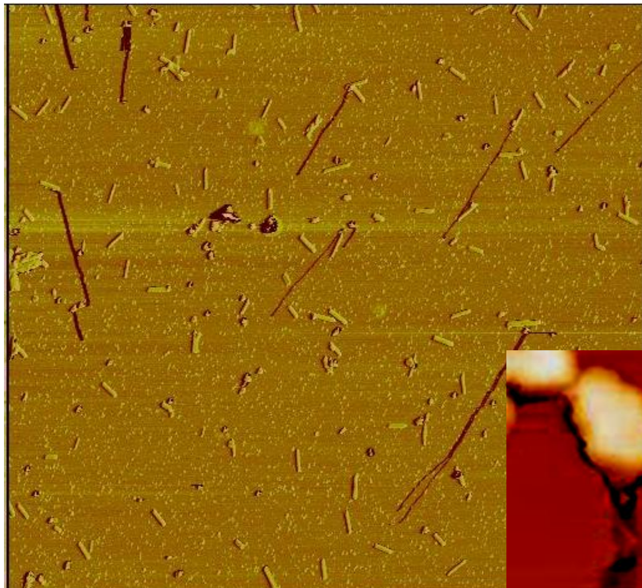
Typical trajectories of bare gold nanoparticles (20 nm diameter)



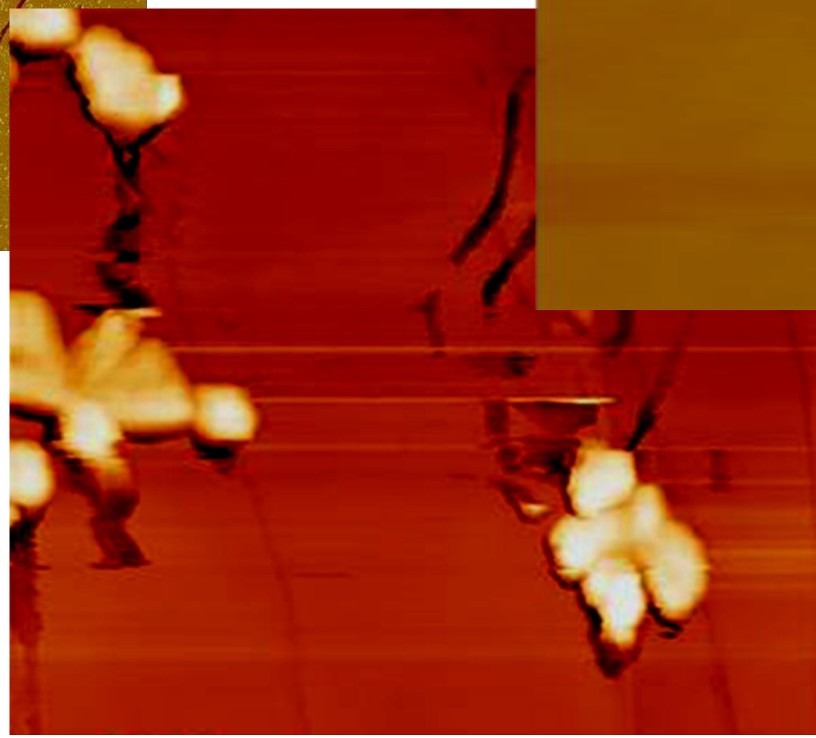
a. low drive amplitude, b. high drive amplitude; scan size: 5µm



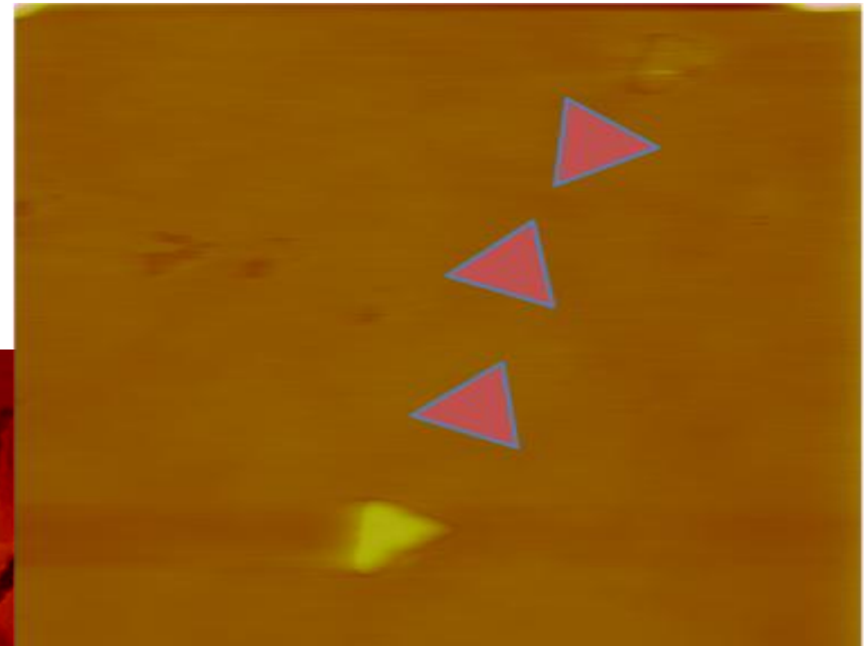
Size and Shape of Au NPs



Nanorods

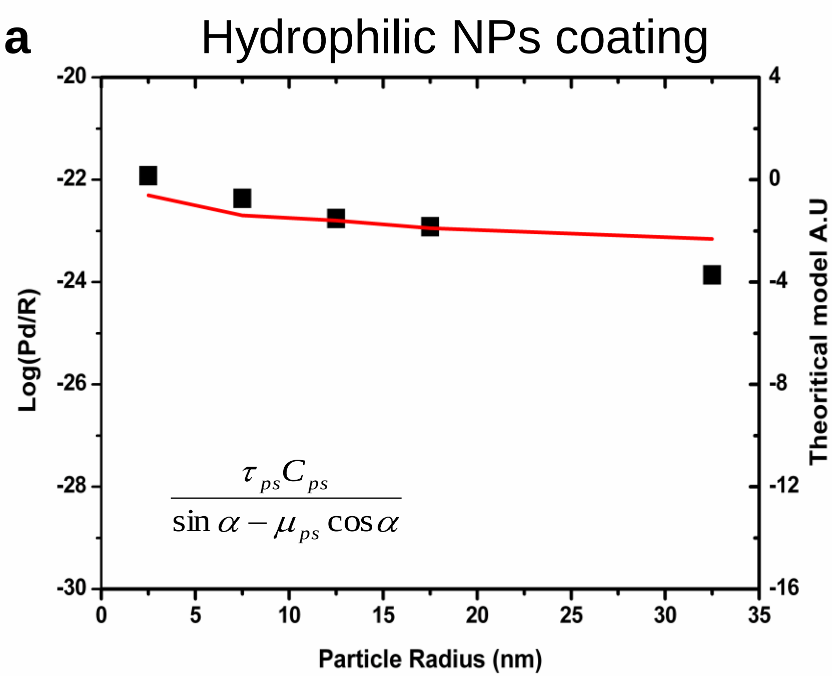


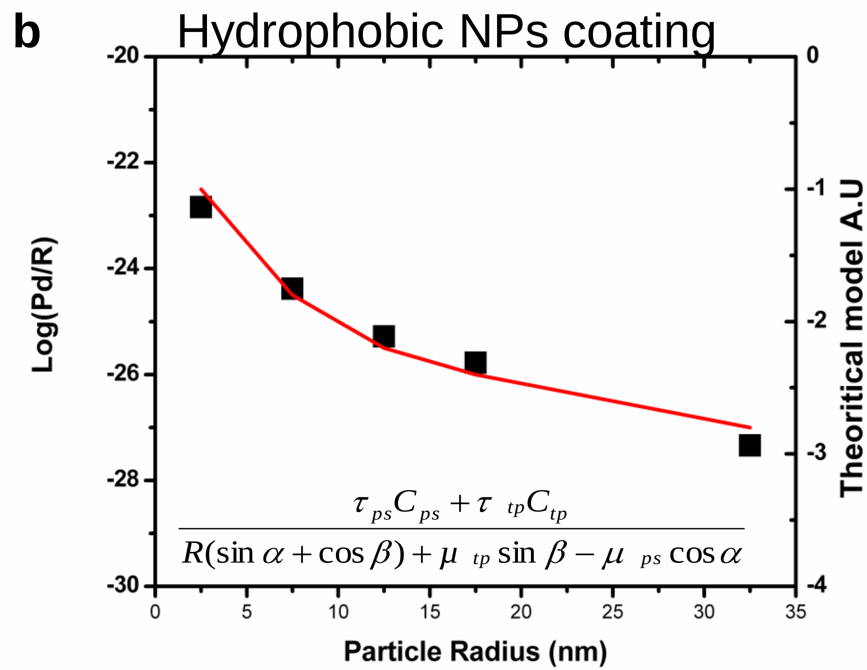
Nanoflowers

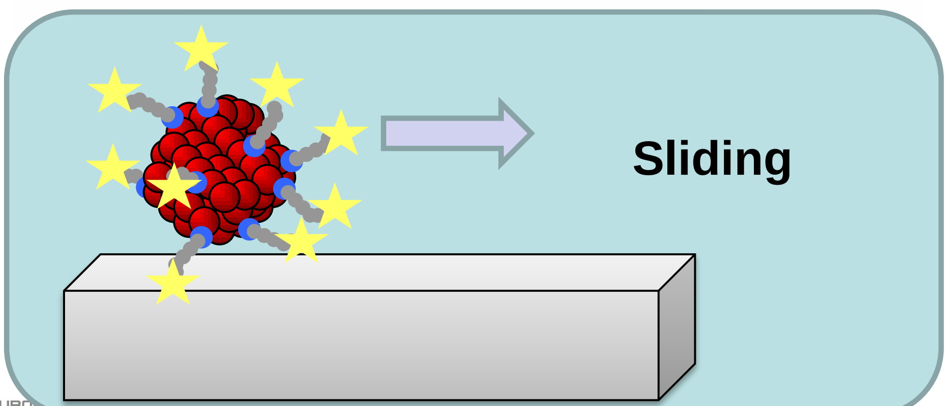


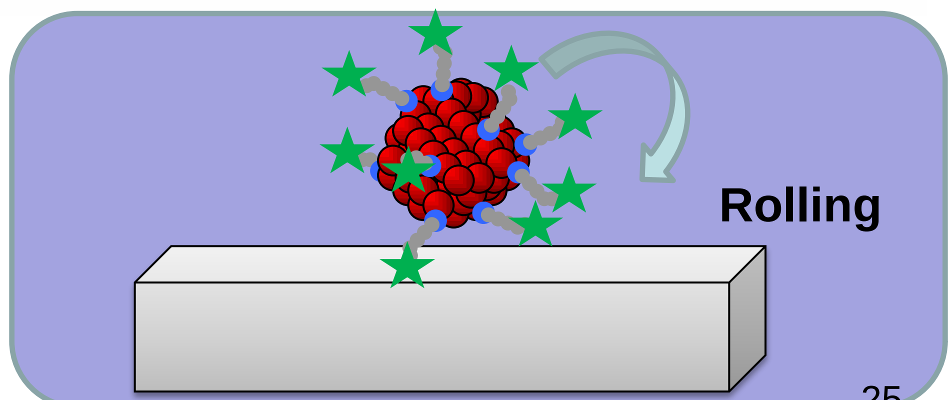
Nanotriangles

Evolution of the logarithm of the dissipated power normalized by the radius (R) of NPs









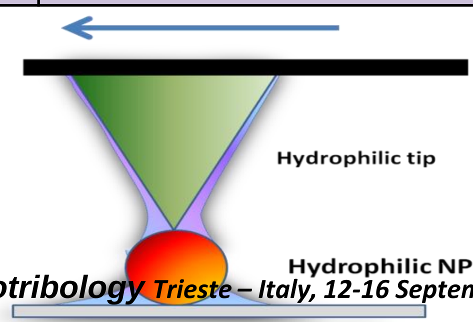
Humidity Rate effect ?

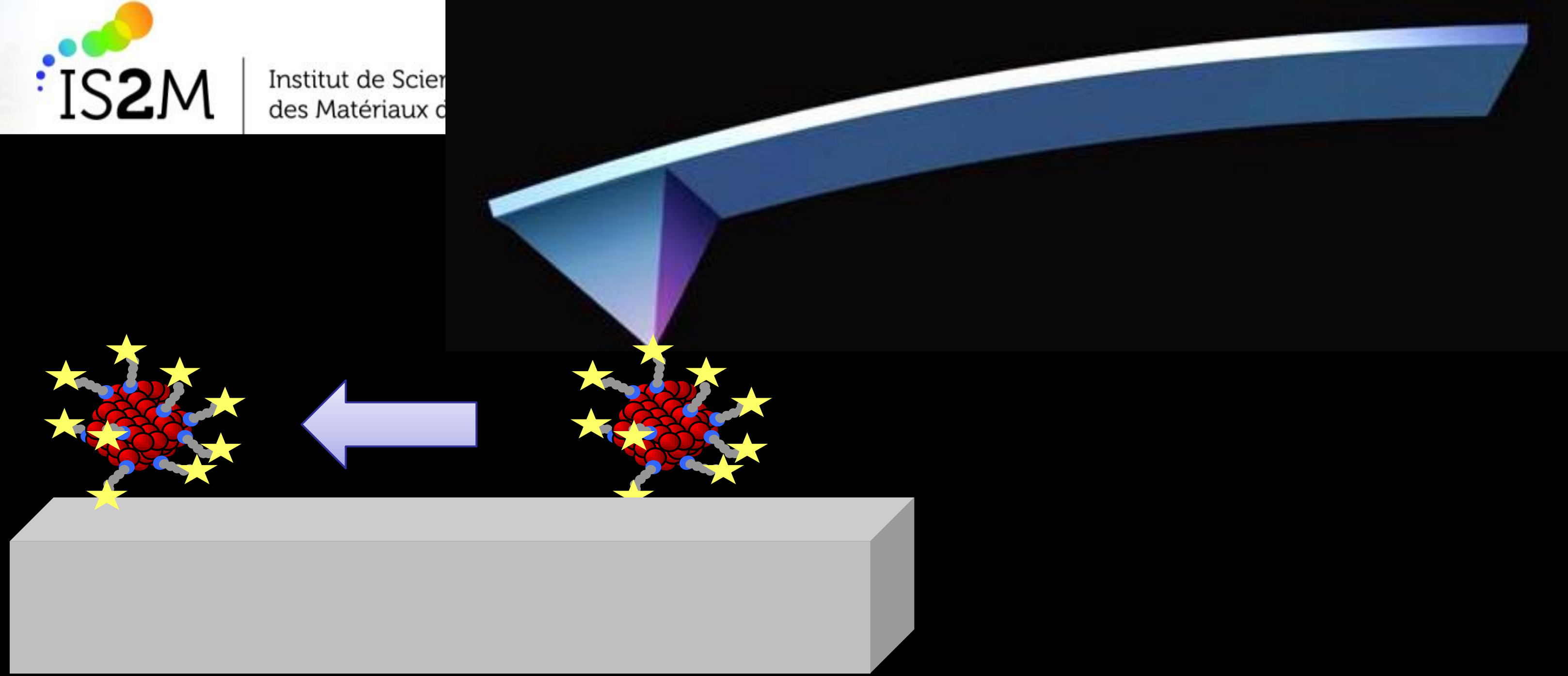
Environment - Humidity Rate

Humidity Rate (%)	33	43	53	
As-synthesized Au NPs on SiO_2	movement	fixed	fixed	1
CH3 coated Au NPs on SiO_2	movement	movement	movement	2
As-synthesized Au NPs on Si-CH_3	movement	movement	movement	3

Ellipsometry results
≠ substrate chemistry and ≠ Relative humidity

Humidity Rate (%)	≤ 33	≥ 53
Condensed Water thickness on SiO_2	1nm <	130 nm
on $Si\text{-}CH_3$	1nm <	1nm <





Friction force F_f = threshold lateral force required to slide the contact between two surfaces

$$F_f \sim \mu(F_{ext} + F_{adh} + F_c)$$

-F_f represent the friction force,

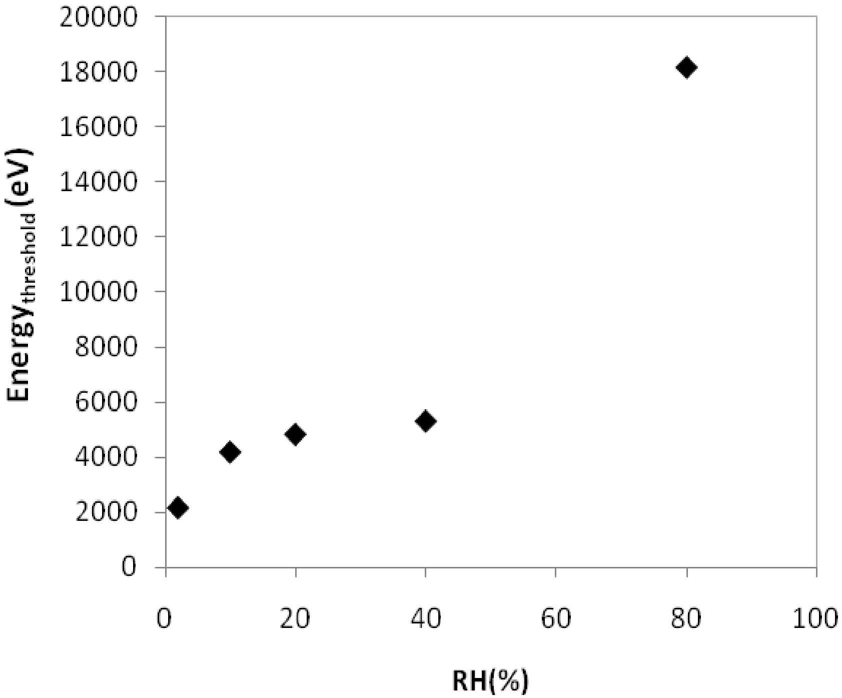
-F_{ext} corresponds to the applied external load,

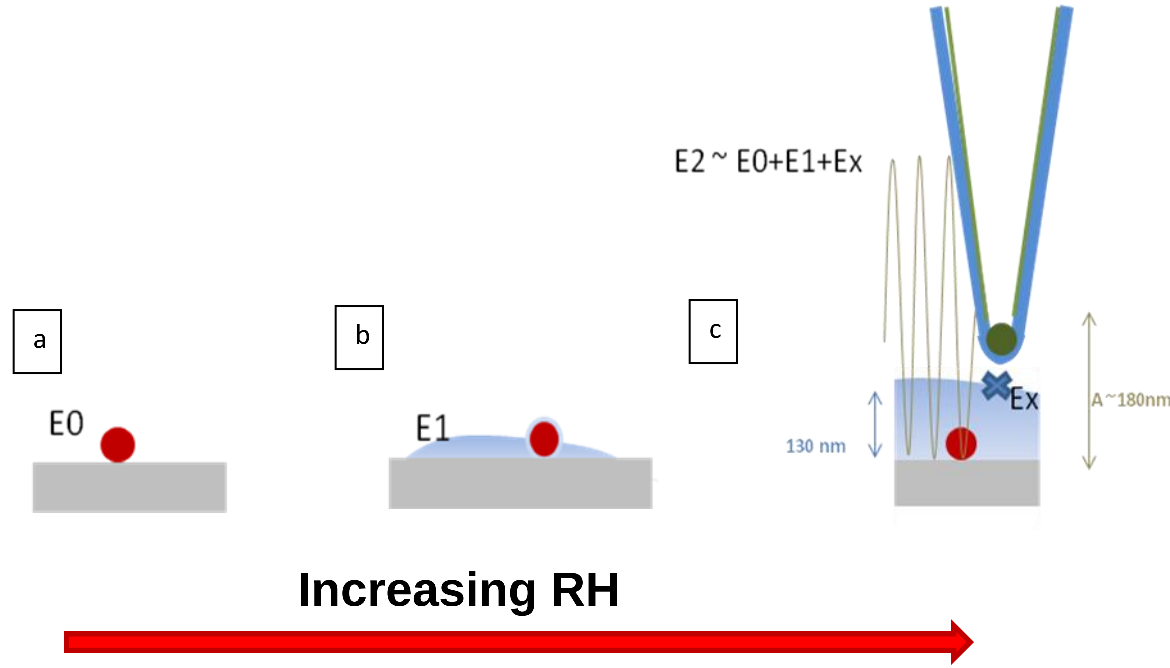
- F_{adh} is the intermolecular adhesion force,

- F_c is the capillary condensation force when its exists

- and, μ is the friction coefficient between surfaces.

Hydrophilic NP - Partially hydrophilic substrate

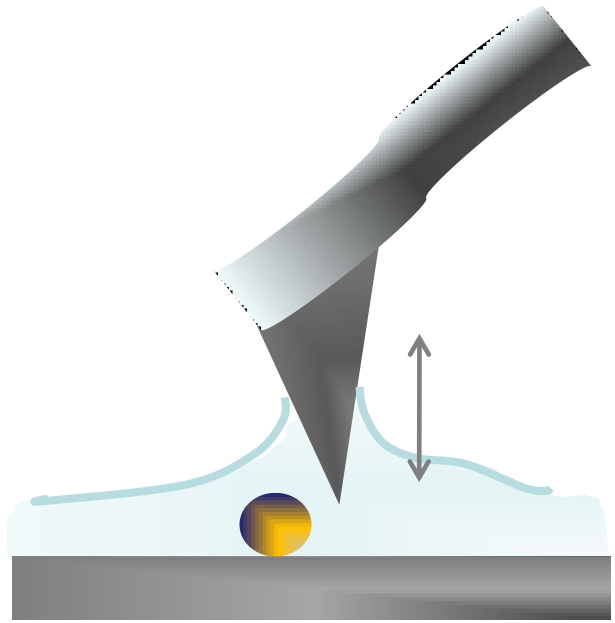




Evolution of the threshold energy dissipation (eV) to move citrate coated NPs (hydrophilic) on SiO_2 (partially hydrophilic) vs the relative humidity.
At 2 % of RH the pressure was 10 mbar and it is the reference value to move these NPs on such substrates.

Schemes of the system configuration (hydrophilic particle/ partially hydrophilic substrate/ partially hydrophilic tip) at different values of relative humidity.
a) RH at 2 % (P=10 mbar), b) RH (10 to 40 %) (P= 10^3 mbar) and c) RH at 80 % (P= 10^3 mbar).

Hydrophilic NP - Partially hydrophilic substrate



TIP Oscillation (Tap) → Energy →
Dissipation in Water → Fixed NP

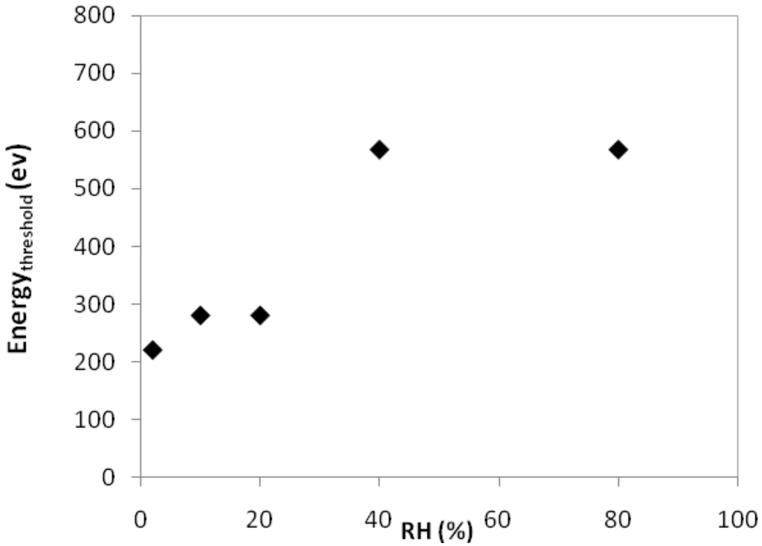
capillary bridging force

$$F_c \sim 2pR_T\gamma_L(\cos\theta_{SL} + \cos\theta_{TL})$$

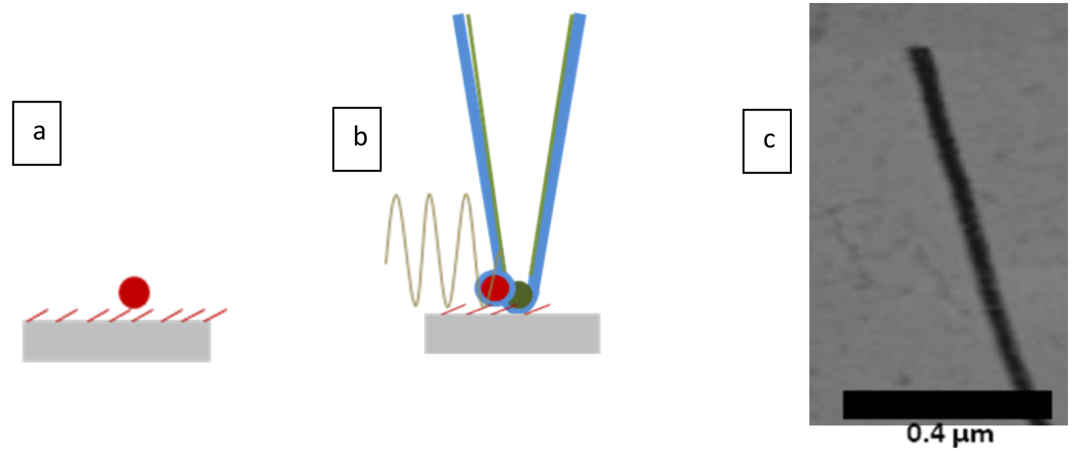
where R_T is the tip radius, θ_{SL} and θ_{TL} are respectively the static contact angles of the liquid on substrate and tip, a nd γ_L is the liquid (water) surface tension

3

Hydrophilic NP - Hydrophobic substrate



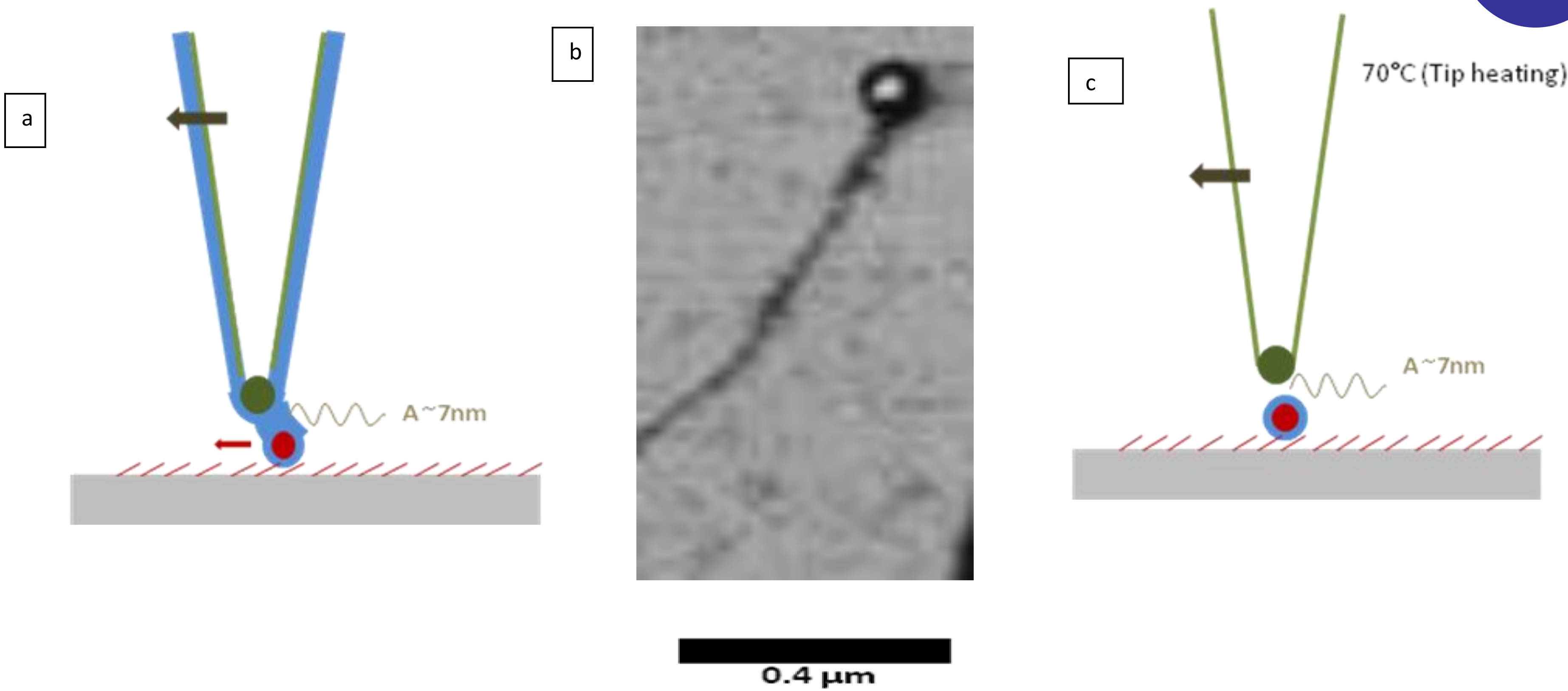
Evolution of the threshold energy dissipation (eV) to move citrate coated NPs (hydrophilic) on silicon wafer coated with –CH_3 terminated groups (hydrophobic coating) vs the relative humidity of the manipulation chamber



Schemes of the system configuration (hydrophilic particle/ hydrophobic substrate/ partially hydrophilic tip) at different values of relative humidity.

a) RH at 2 % (P=10 mbar), b) RH (10 to 80 %) (P= 10^3 mbar).
b) c) AFM phase image in Tapping mode, during
c) the manipulation of NP; the black line corresponds
d) to the trajectory of the particle (slow scan axis down).

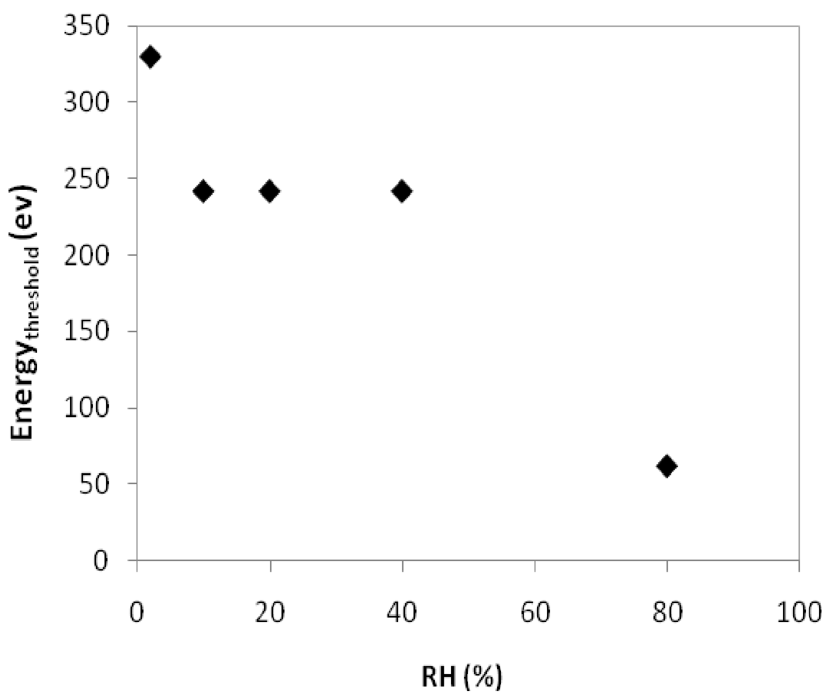
Hydrophilic NP - Hydrophobic substrate

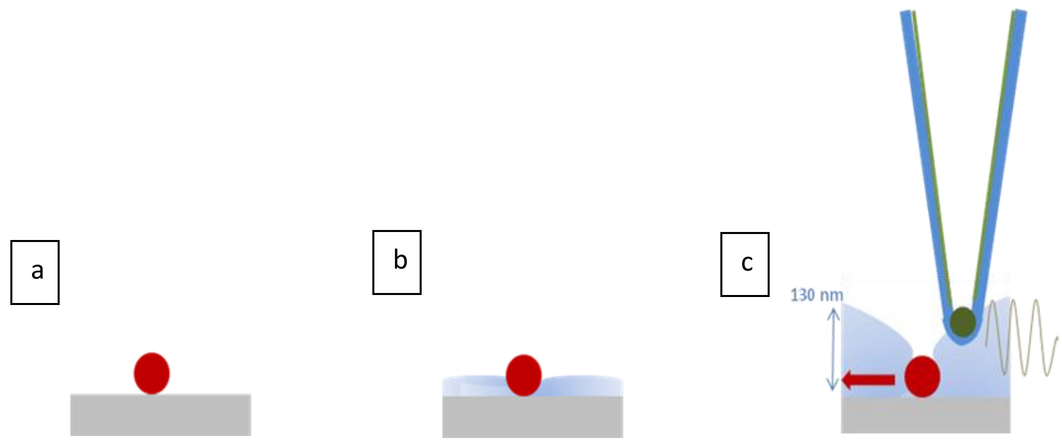


Schemes of the system configuration (hydrophilic particle/ hydrophobic substrate/ partially hydrophilic tip) at 80 % of RH using low A_{set} and drive amplitude (tapping parameters): a) tip pulling NP via the capillary bridge between the tip/NP and c) fixed NP after heating of the tip. b) AFM phase image in tapping mode, during the manipulation of NP; the black line corresponds to the trajectory of the particle (slow scan axis down).

Hydrophobic NP - Partially hydrophilic substrate

2





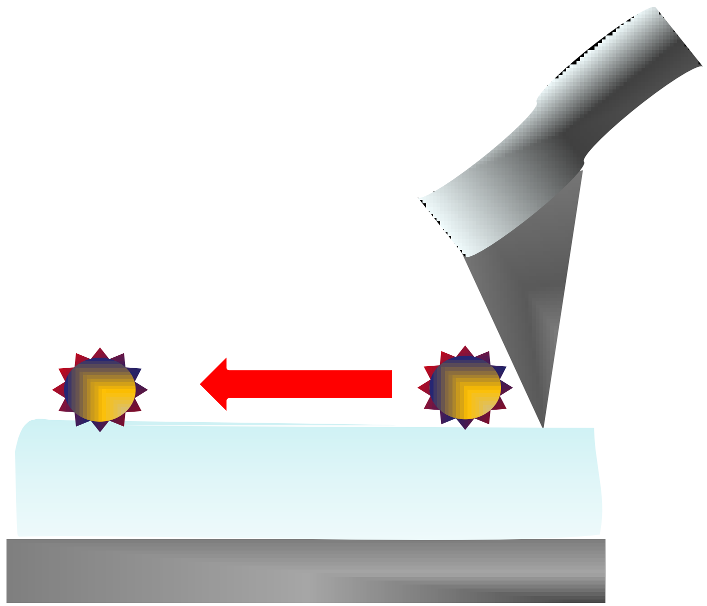
: Schemes of the system configuration (hydrophobic particle/ partially hydrophilic substrate/ partially hydrophilic tip) at different values of relative humic
a) RH at 2 % (P=10 mbar), b) RH (10 to 40 %) (P= 10^3 mbar) and c
b)) RH at 80 % (P= 10^3 mbar).

Evolution of the threshold energy dissipation (eV) to move methyl coated N Ps (hydrophobic) on silicon wafer (partially hydrophilic) vs relative humidity.

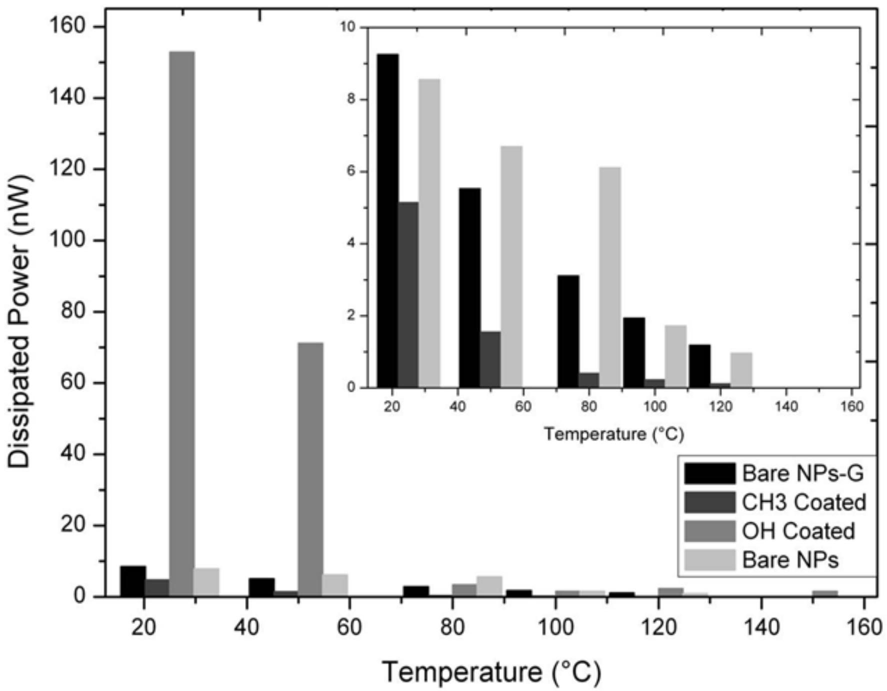
Hydrophobic NP - Partially hydrophilic substrate

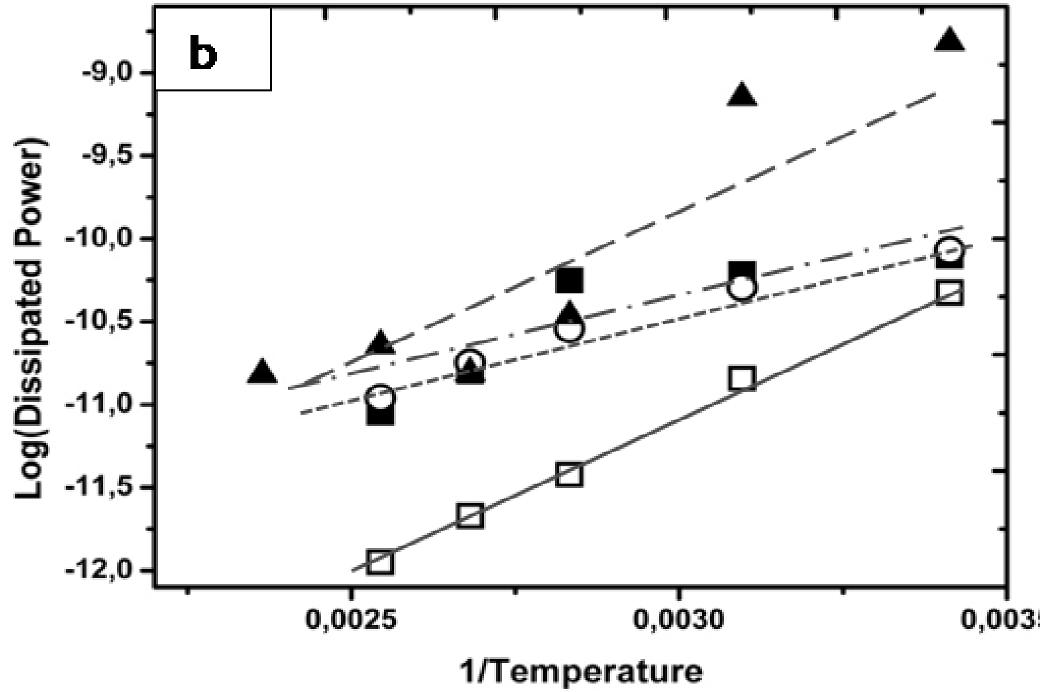
2

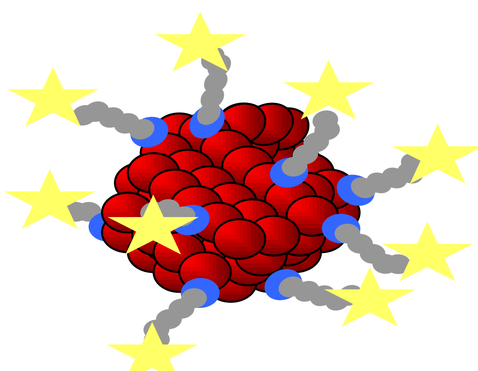
*Hydrophobic NP
*Partially hydrophilic
substrate



Environment - Temperature







■ raw nanoparticules,

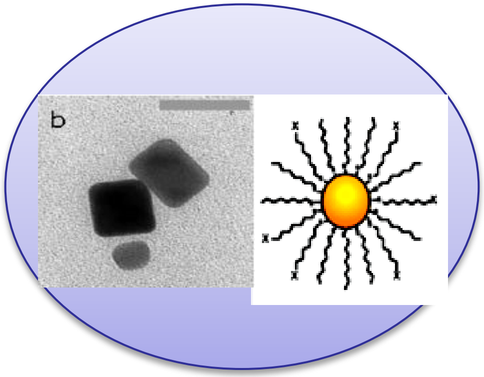
○ raw nanoparticles geometrically organized,

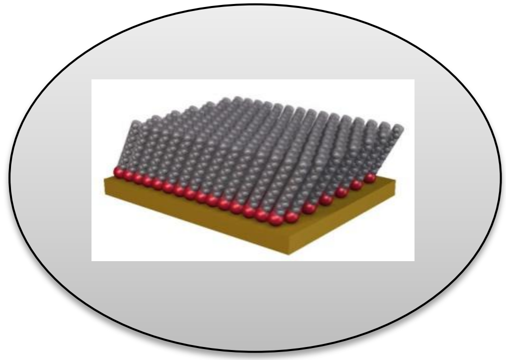
□ CH_3 coated nanoaprticles ,

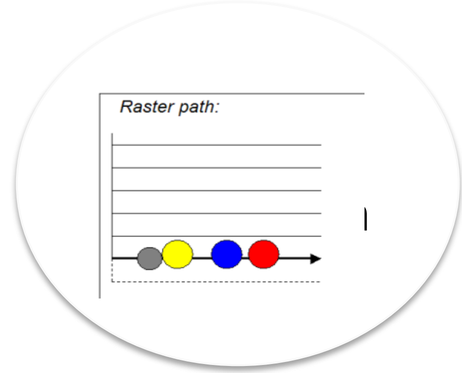
▲ OH coated nanoparticles

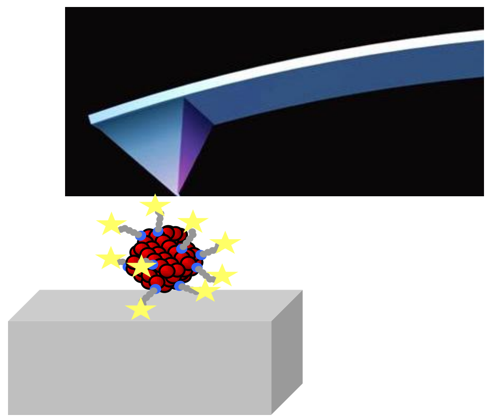
K. Mougin et al Langmuir 2008, 24, 1577.

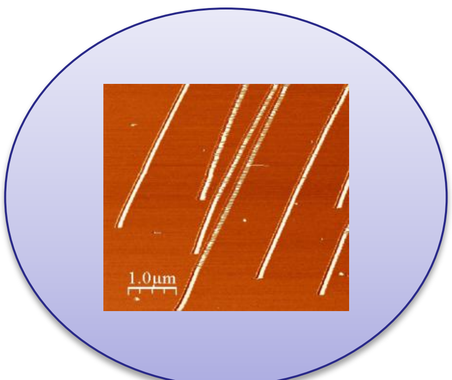
Conclusion

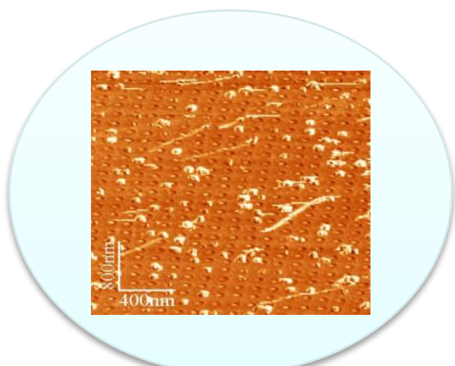


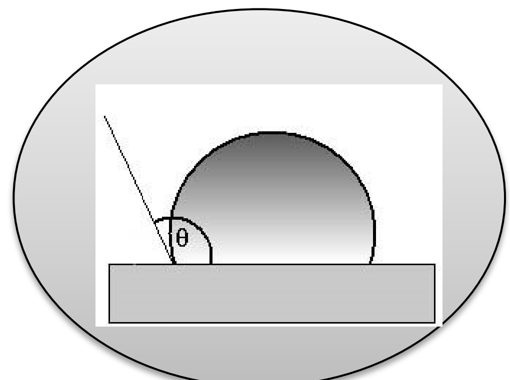




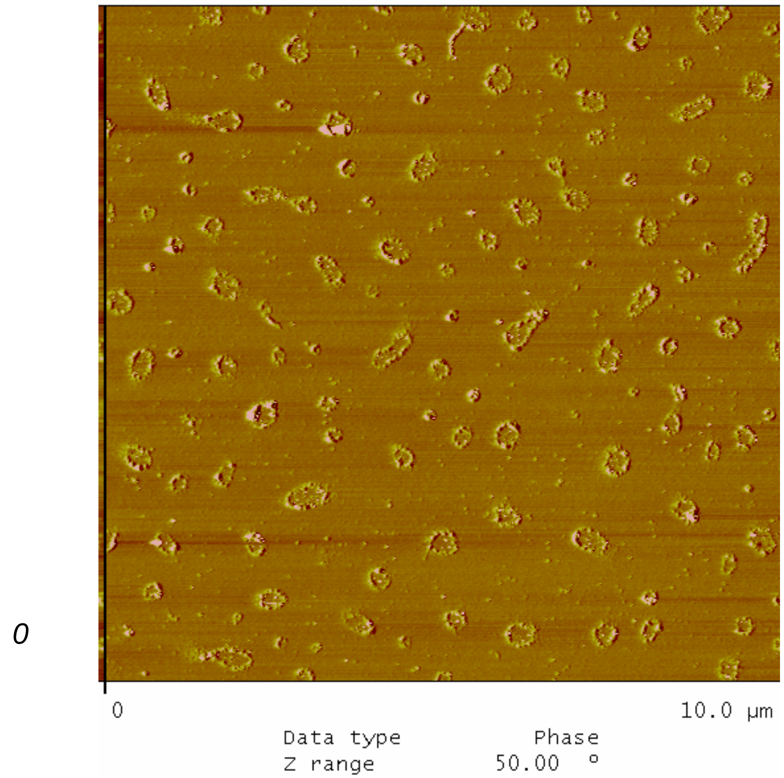




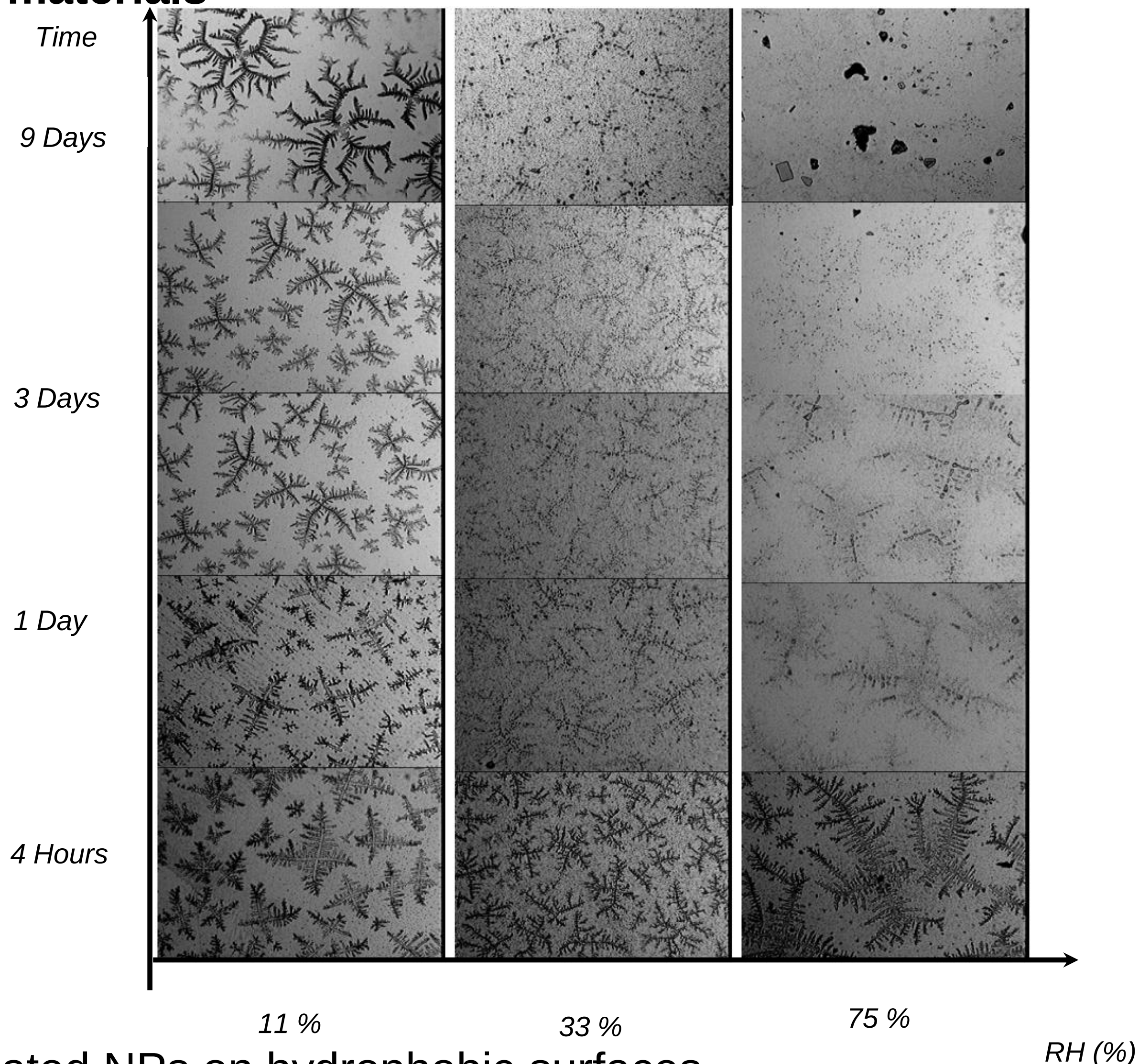




Stability of NPs based materials

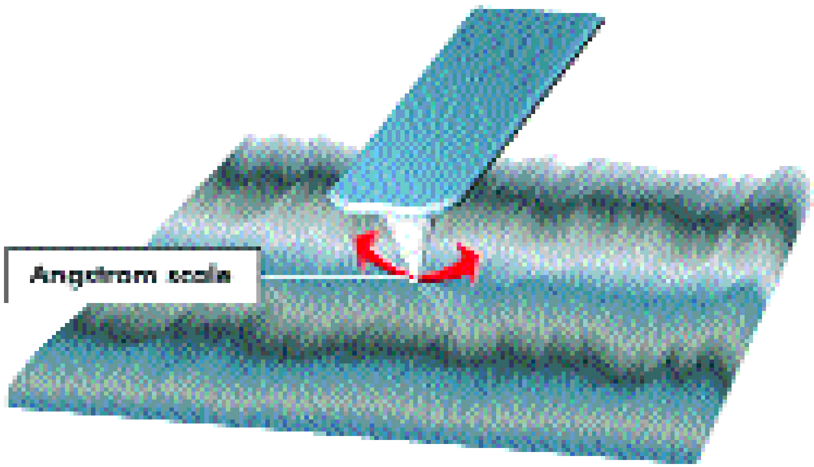


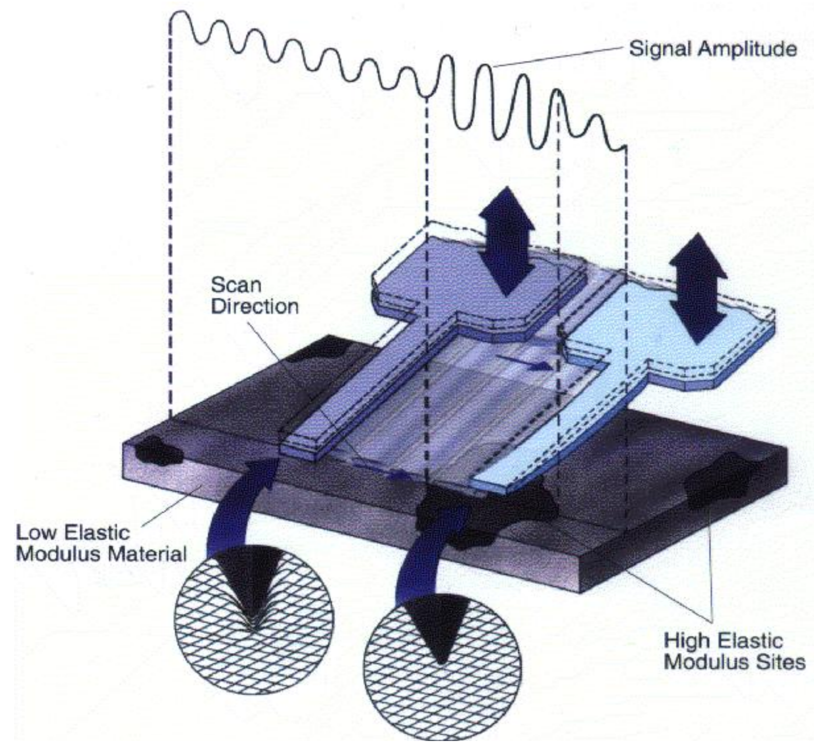
After several months



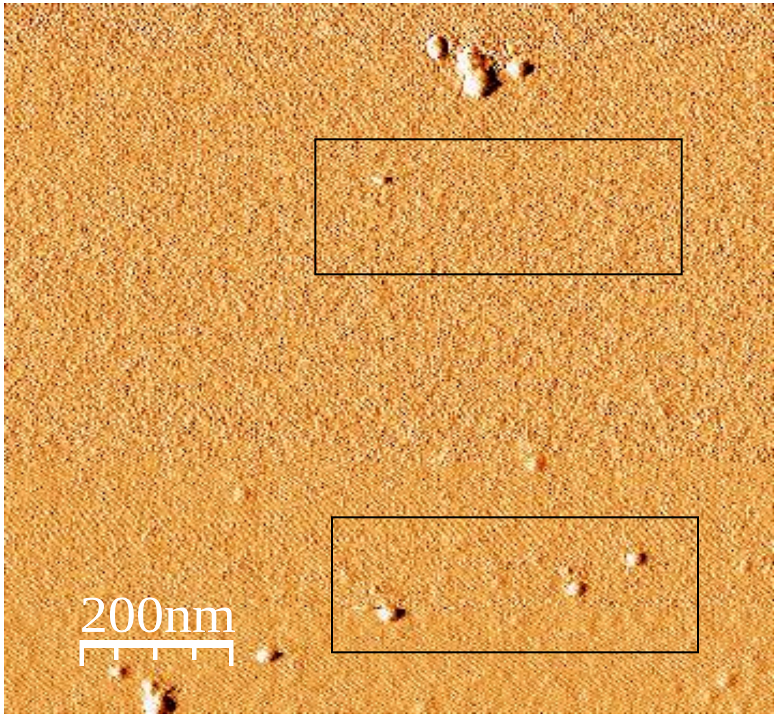
Solutions: **Hydrophobic** coated NPs on hydrophobic surfaces

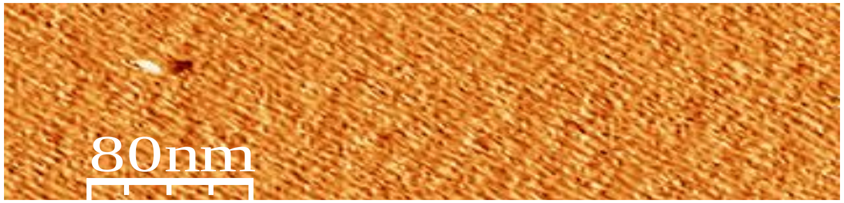
Torsion Mode.. & Particle fly away…

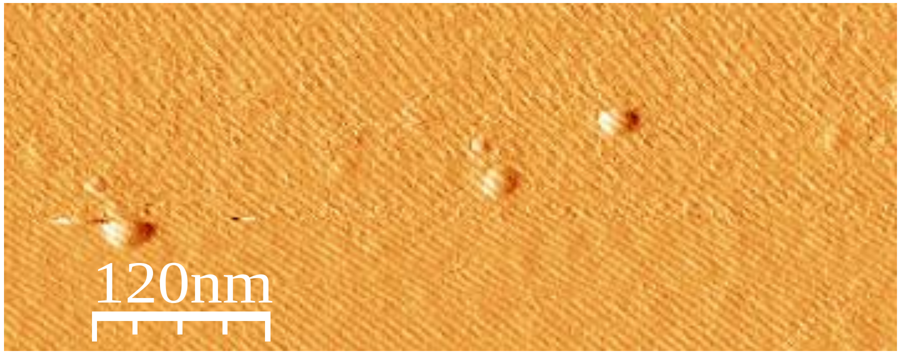




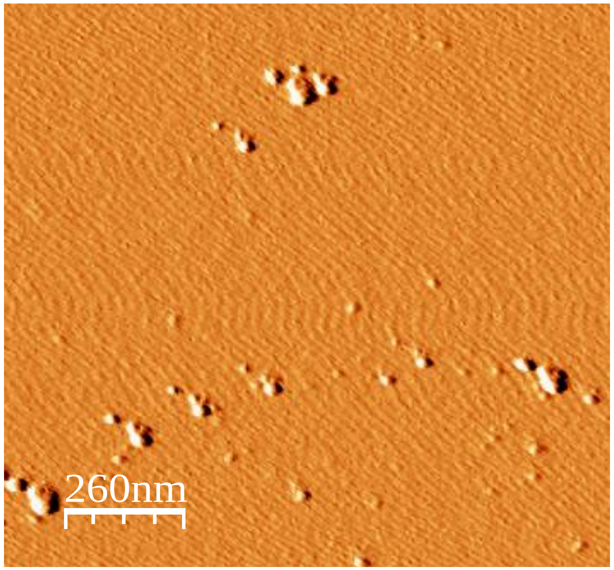
Techniques –Torsion Mode



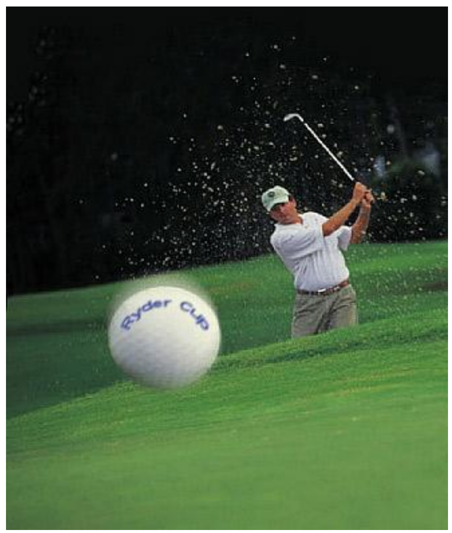


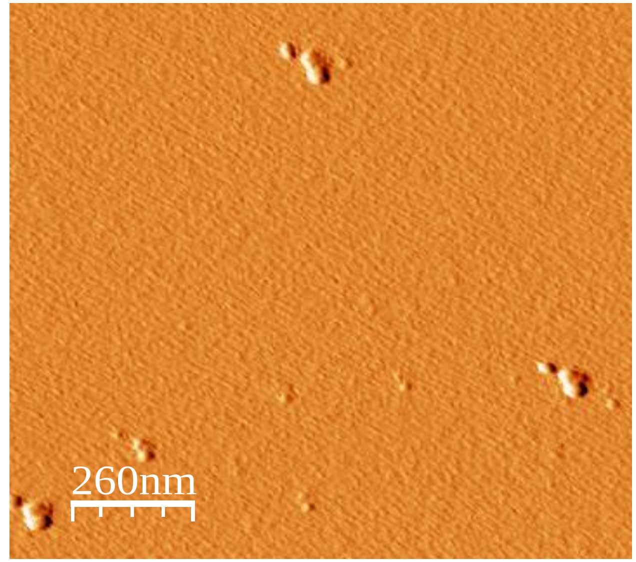


Nano-golf?



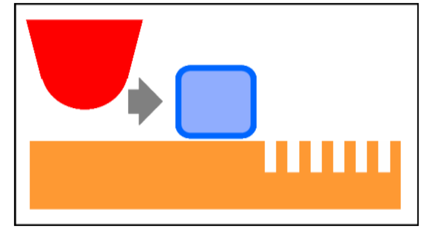
Before





After

Aknowledgements



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Thank you