Nanostructures based on metallic nanoparticles and biomolecules

Research topics:

- *Hybrid nanostructures based on metallic nanoparticles and biomolecules (amino acids, DNA)*
- *Usage of hybrid nanostructures in microelectronics and sensor devices*

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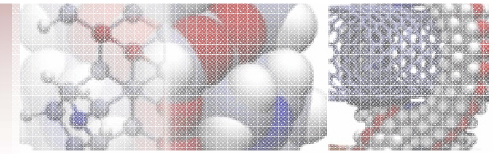
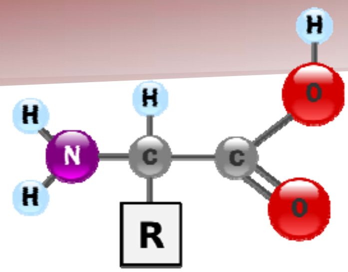
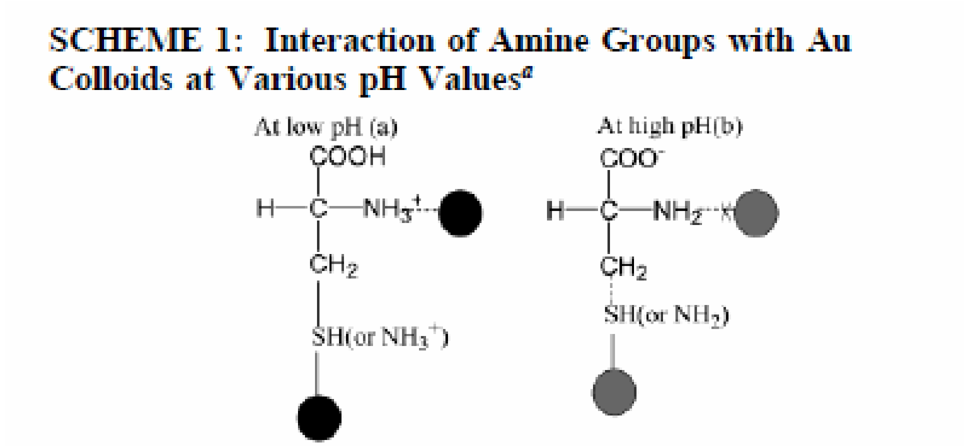
Amino Acids

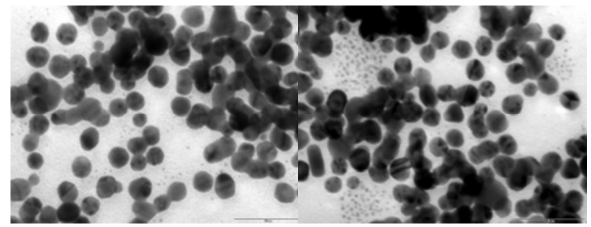




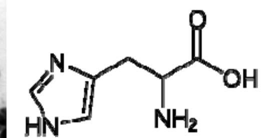
Amino acids are molecules containing an amine group, a carboxylic acid group and a side-chain that varies between different amino acids

They are the building blocks of proteins, which are linear chains of amino acids



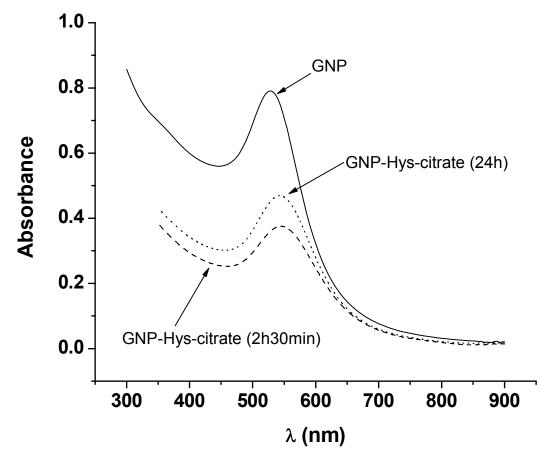


Hysidine capped gold nanoparticles

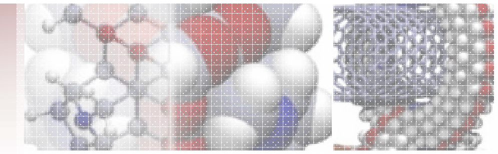


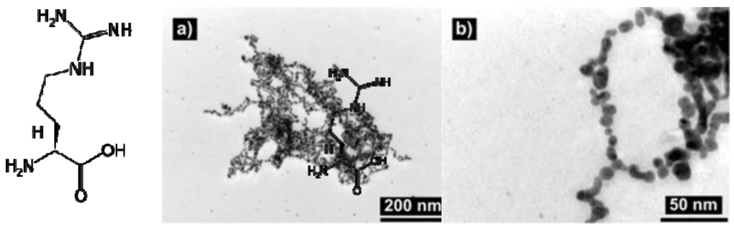
L-hystidine

Colloidal solution of amino acid capped gold nanoparticles

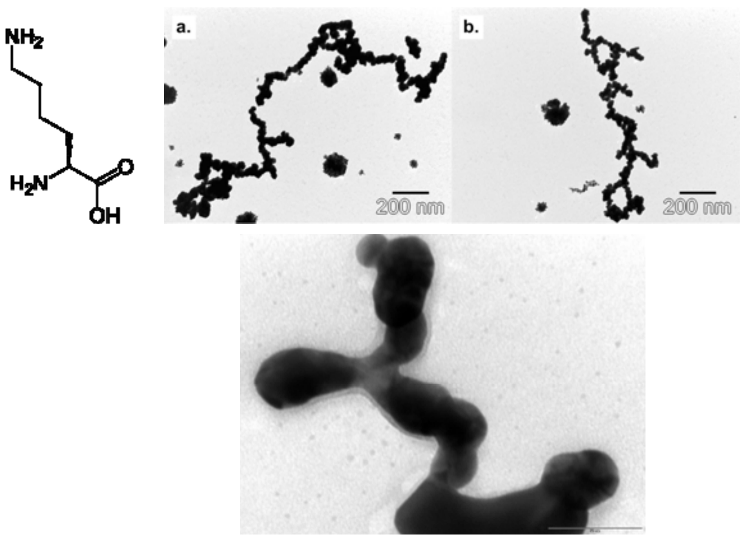


UV-Vis spectra of hystidine-capped gold nanoparticles (exhibits a single plasmon resonance band)

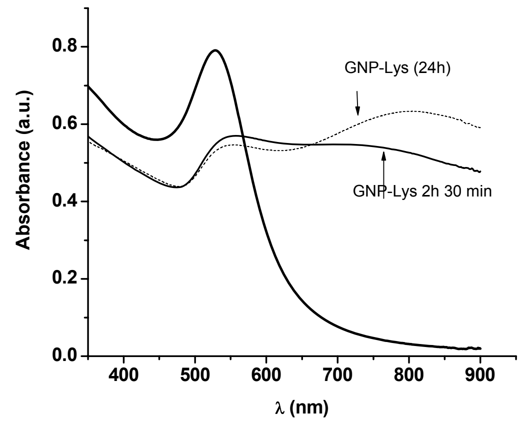




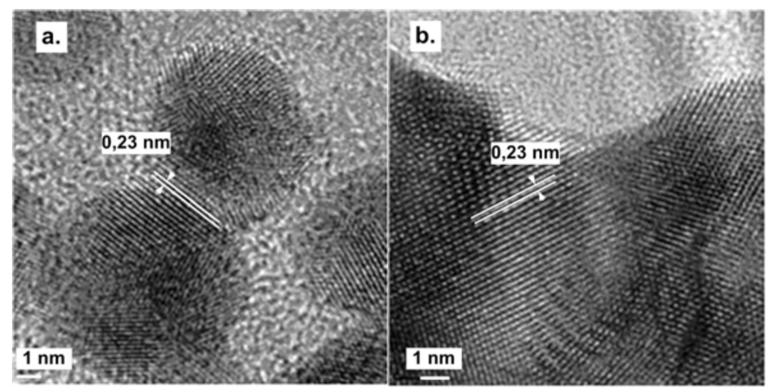
Arginine capped gold nanoparticles



Lysine capped gold nanoparticles

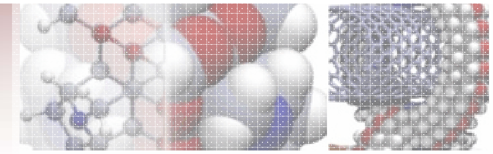


UV-Vis spectra of lysine-capped
gold nanoparticles (exhibits two plasmon resonance bands)



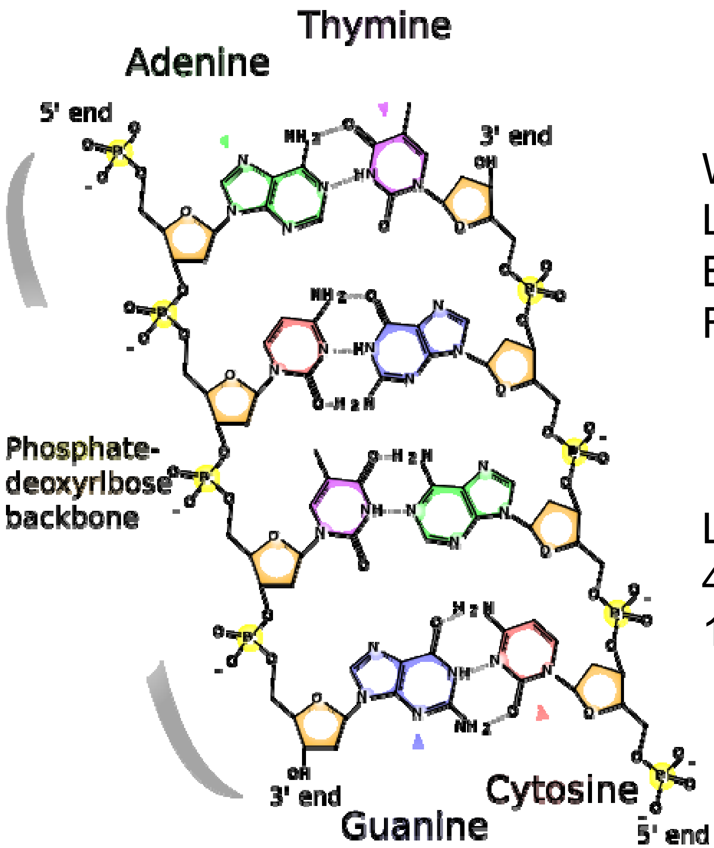
HR-TEM of lysine-capped gold nanoparticles
(the fusion between nanoparticles take place along (111) plane)

S. Pruneanu et al. J Mater Sci (2010) 45:3151–3159



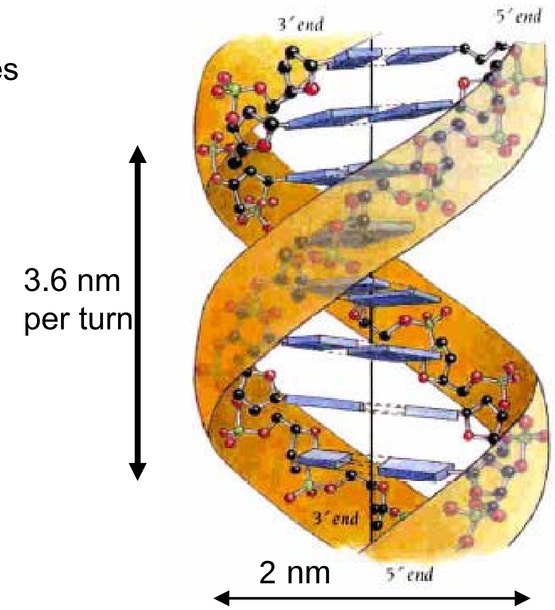
DNA

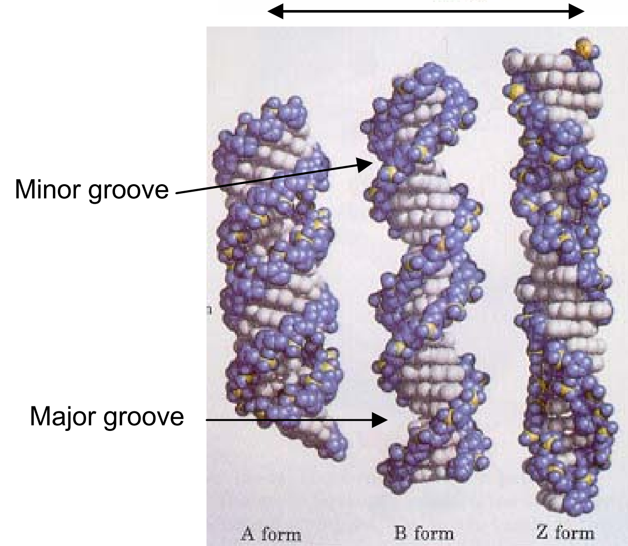
DNA molecules can be successfully used as a template to create nanowires



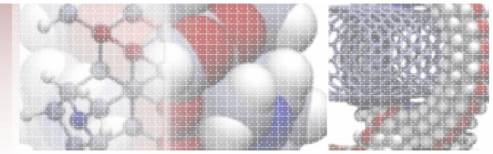
Width: 2 nm
Length: nm, µm, m
Base pairs: AT, GC
Flexibility

Lambda-DNA
48500 base pairs
15 microns long

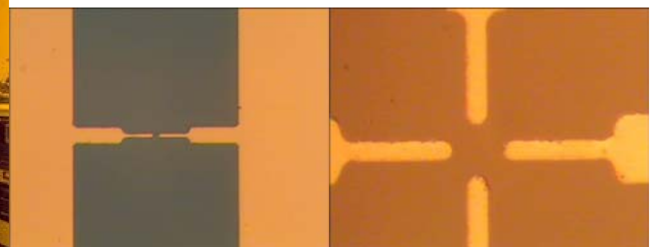




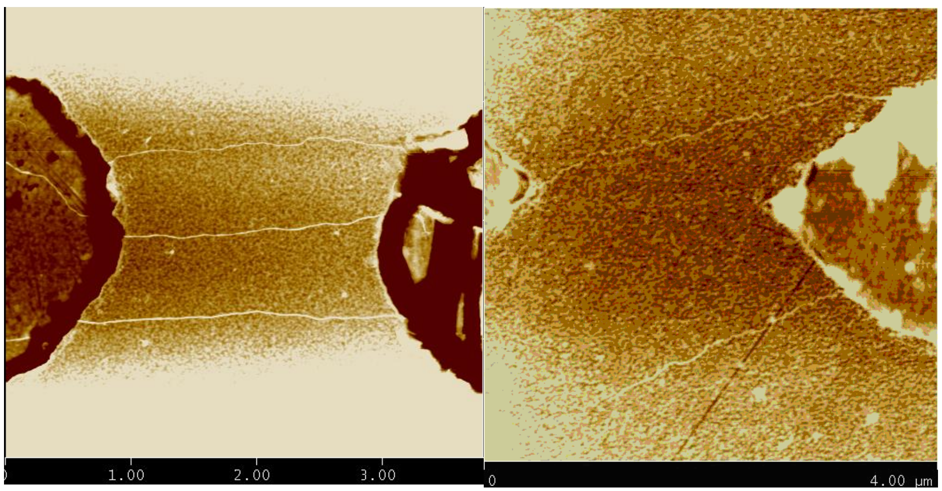
DNA as nano-connector



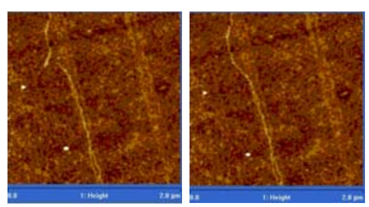
Clean-room



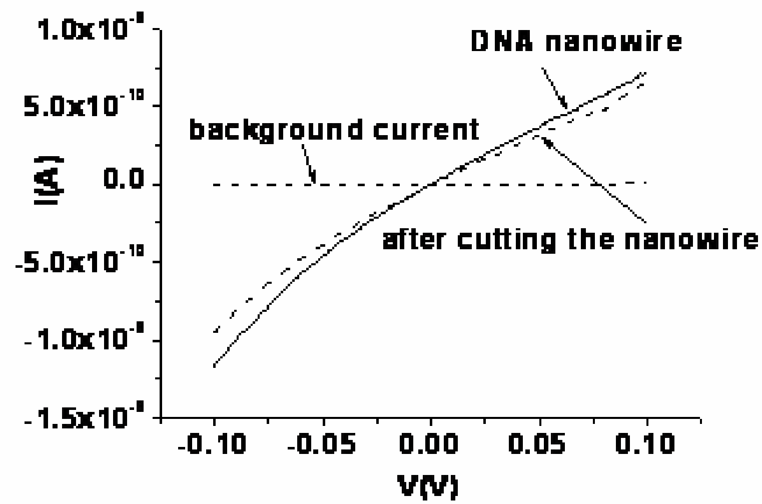
Microelectrodes prepared by photolitography



DNA molecules connecting gold microelectrodes (3 micrometer apart)

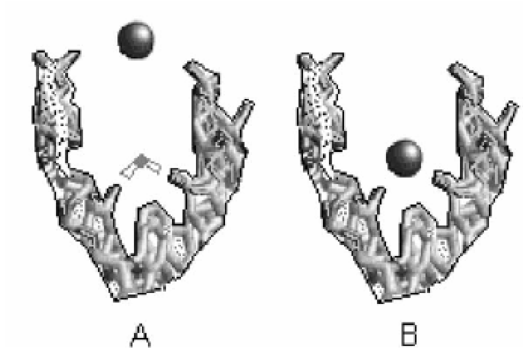


DNA molecule cut with the cantilever

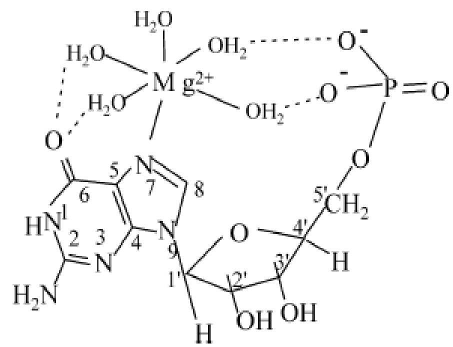


I-V curve of a single DNA molecule, attached between gold microelectrdes (no current is recorded through DNA molecule)

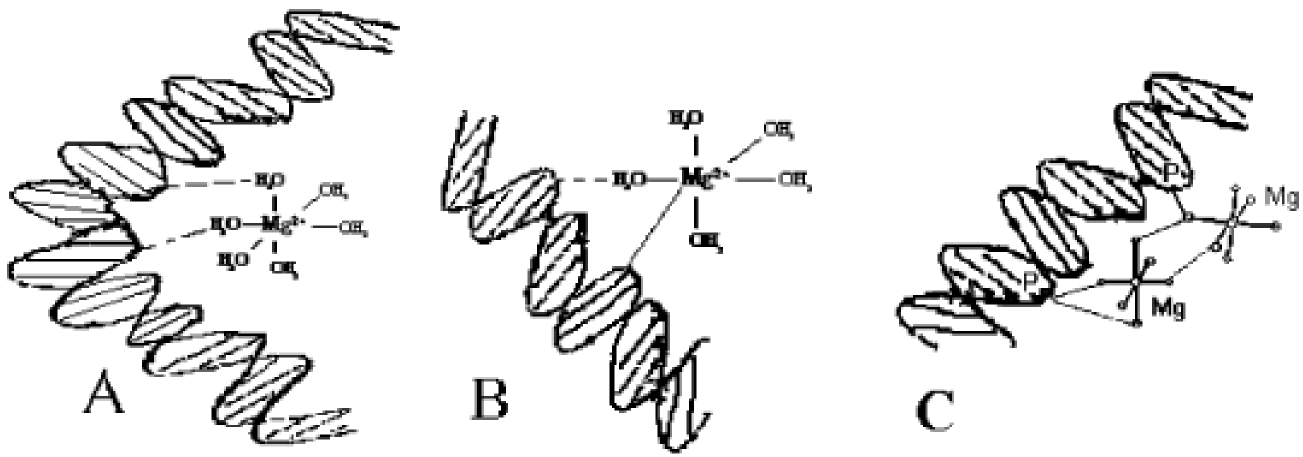
Interaction between metals and DNA



Monovalent cations (Na+, K+, Cs+)
in the minor groove of DNA



Magnesium binds directly to guanine and indirectly to O6 and phosphate group.



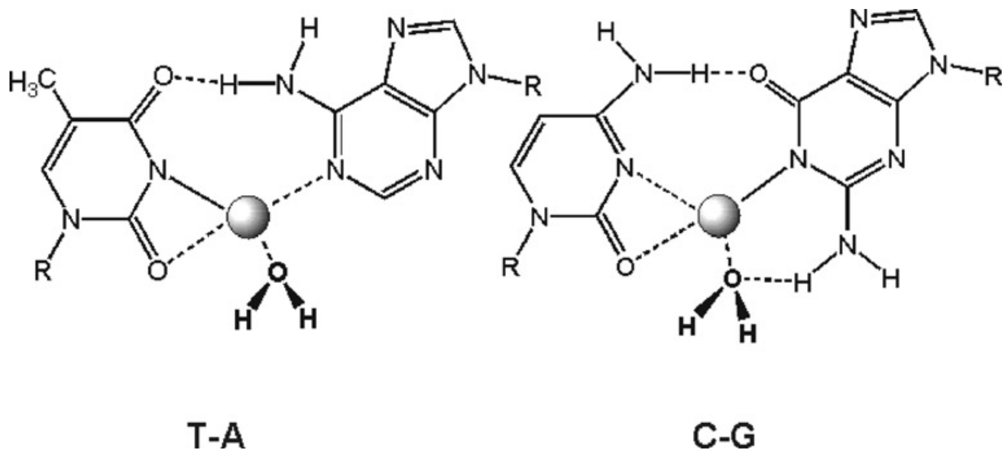
Direct and indirect binding of Mg^{2+} to DNA

Silver-DNA nanowires

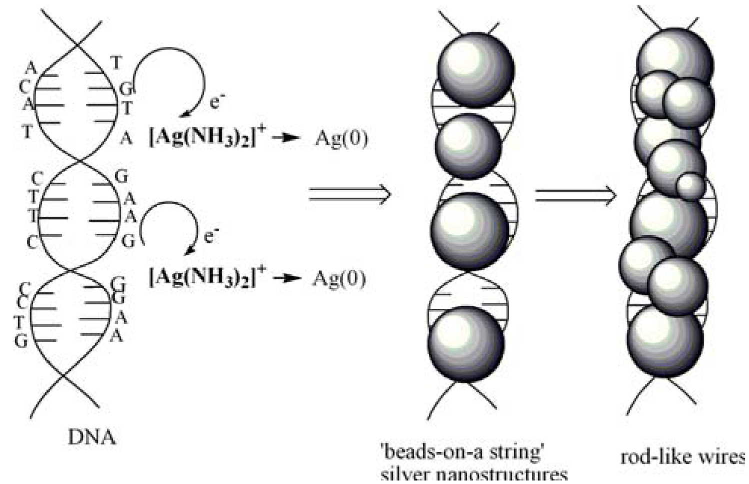
Ag$^+$/nucleotide ratio:

r = 1/80 , Ag$^+$ binds to N7 of guanine

r = 1/2 , Ag$^+$ binds to N7 of adenine

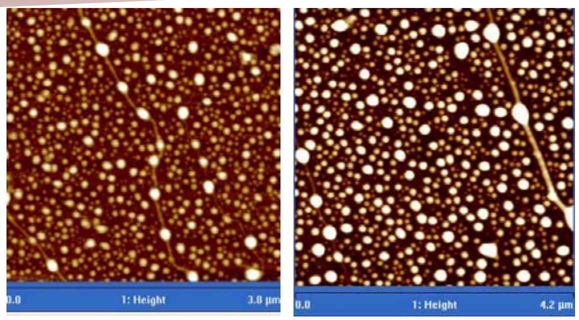


Interaction between Ag$^+$ ions and DNA bases.

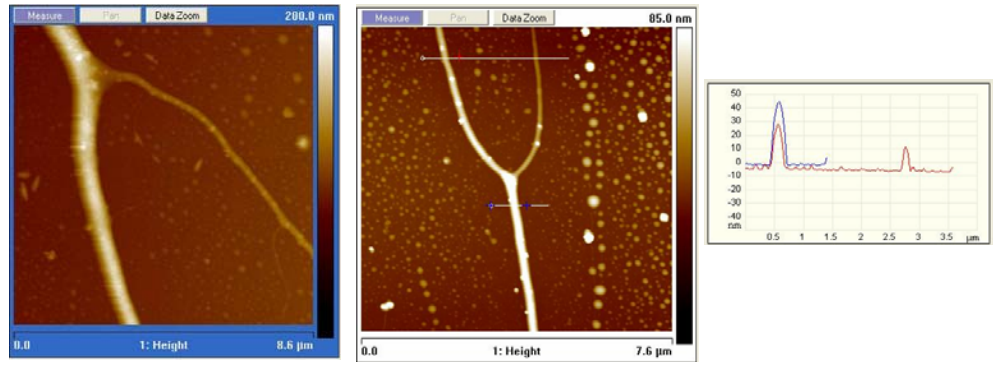


Schematic illustration of the nucleobase redox process: formation of 'beads-on-a-string' silver nanostructures and rod-like wires

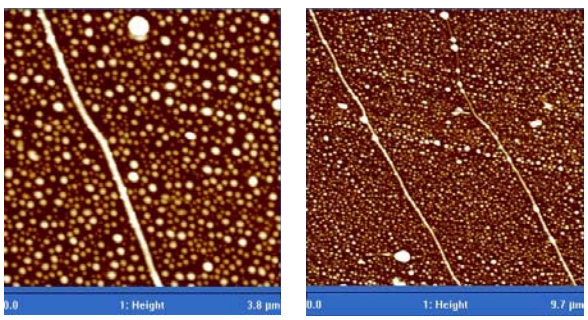
Silver-DNA nanowire morphology and conductivity



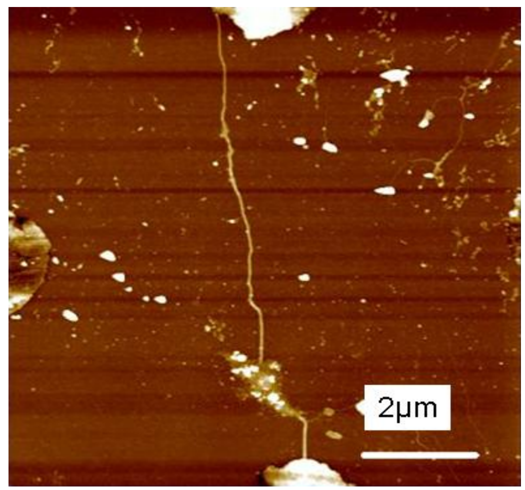
Silver-DNA nanowires
('beads-on-a string' morphology)



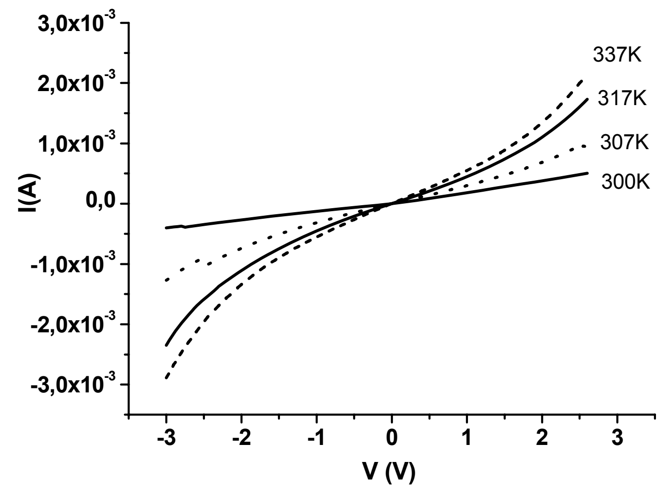
Silver-DNA nanoropes



Silver-DNA nanowires (diameter 10-40 nm)



Silver-DNA nanowire connecting two gold microelectrodes

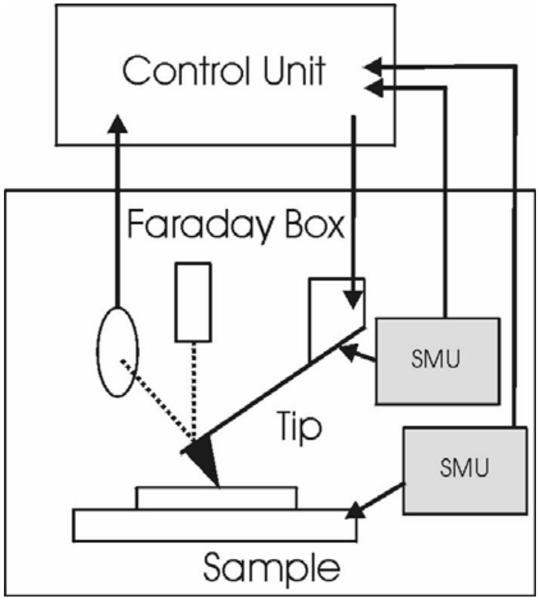


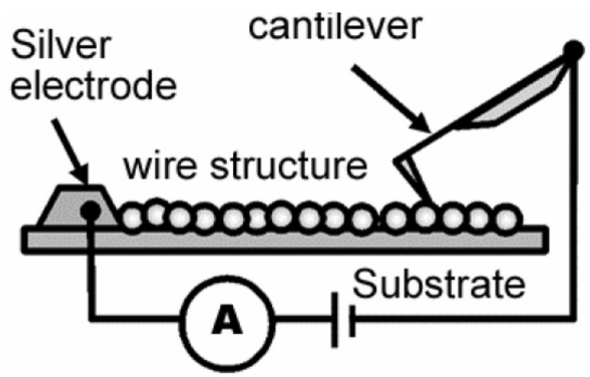
ρ = 1.46 x 10^{-7} Ohm x m- silver nanowire

ρ = 1.6 x 10^{-8} Ohm x m – silver bulk

S. Pruneanu et al. J Mater Sci (2010) 45:3151–3159; Electrochem. Commun. (2009) 11(3) 550-553

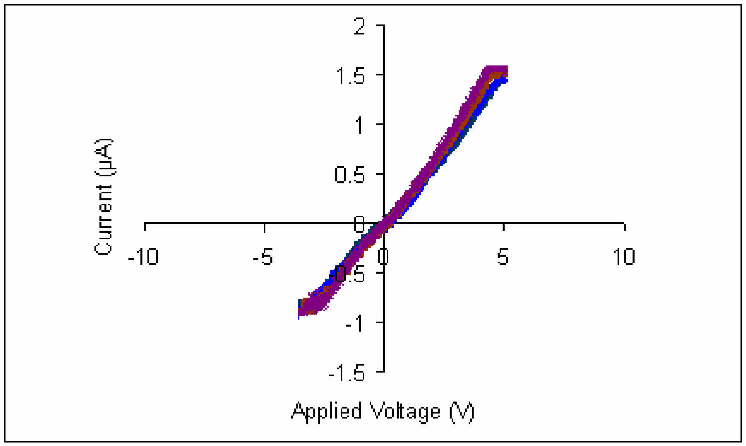
Conductive-Atomic Force Microscopy





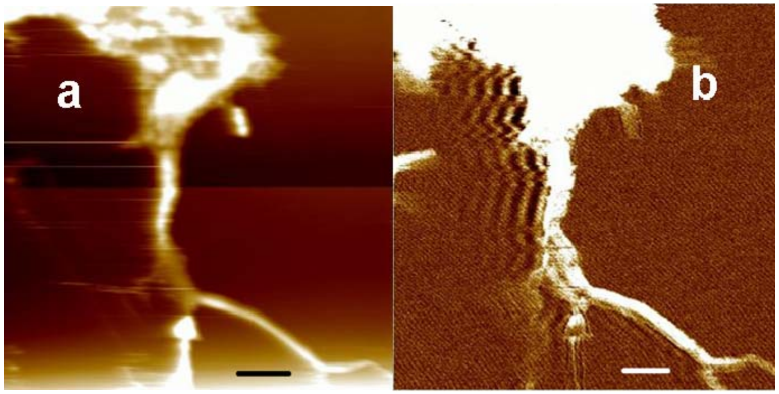
C-AFM experimental set-up

- ❑ Simultaneously maps the topography and the electrical properties of the sample (contact mode)
- ❑ I-V characteristics can be recorded
- ❑ Metal coated cantilevers: Pt, Ir, Co (30-50 nm)
- ❑ Applied voltage: 0 ± 12V

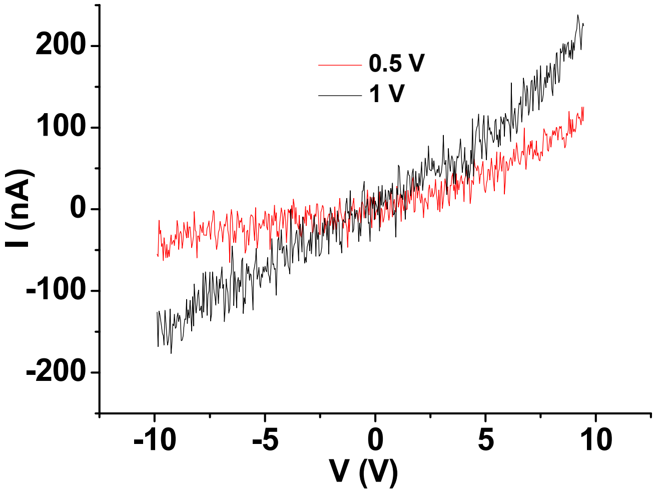


I-V curve recorded with C-AFM

I-V characteristic of silver-DNA nanowire recorded by C-AFM



C-AFM images: topography (a) current map (b)



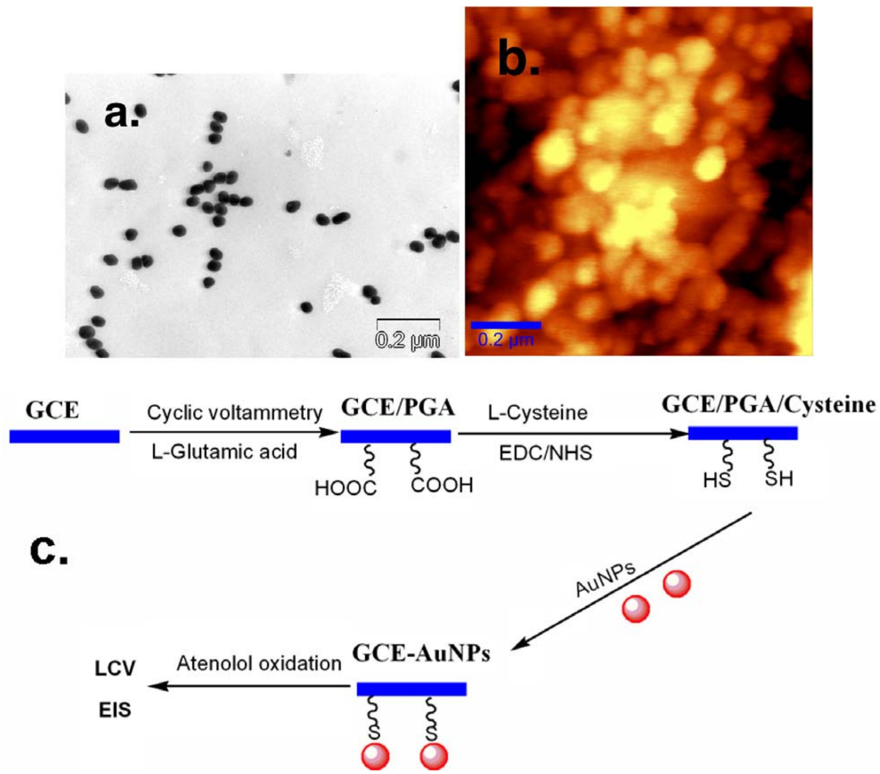
R = 173 M Ω

R = 66 M Ω

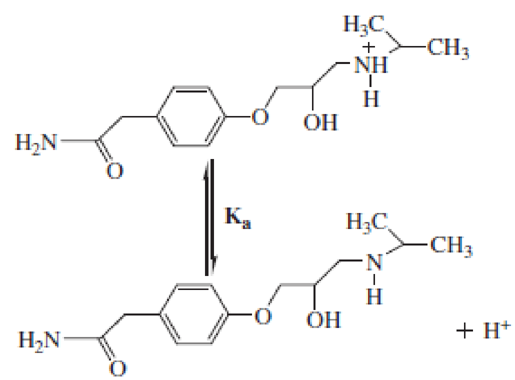
I-V curve obtained with C-AFM, at various external biases: 0.5 v respectively 1V

Nanostructured electrode with electrocatalytic properties

- we can used amino acids to link gold nanoparticles to an electrode surface
- the electrocatalytic properties of such electrode is greatly enhanced
- we have chosen to study atenolol oxidation process



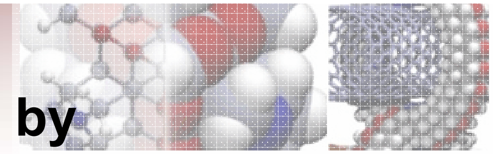
TEM image of dispersed nanoparticles (20-30 nm) (a);
AFM image of nanostructured electrode (b);
Schematic reprezentation of nanoparticles attachement to gold surface (c).



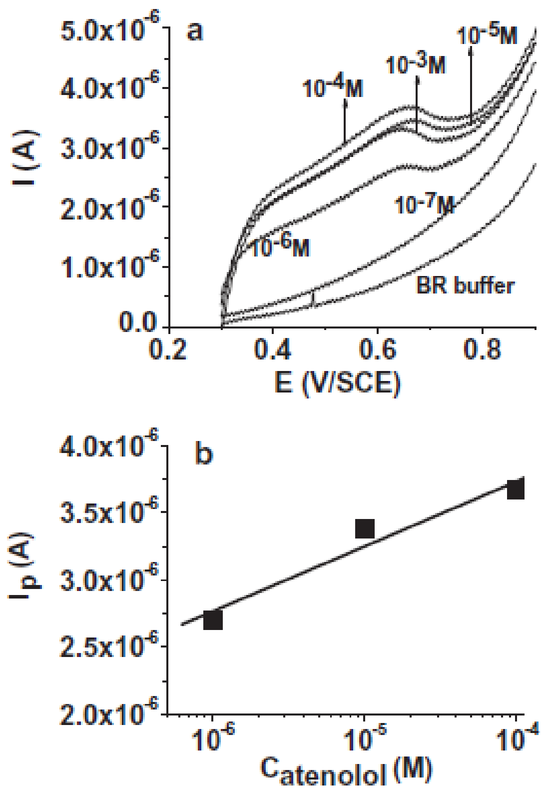
Atenolol is an antihypertensive drug
$pK_a = 9.4$

Oxidation of amino-group takes place at pH >9

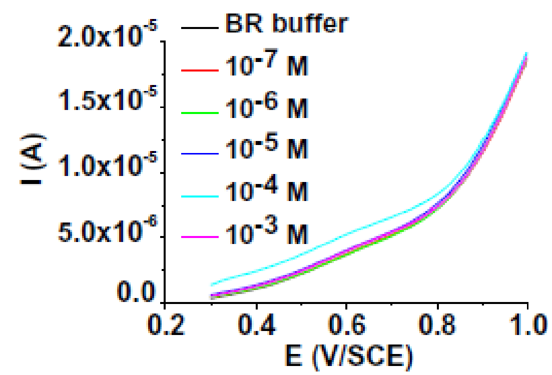
S. Pruneanu et. al, Chemical Physics Letters 504 (2011) 56–61



Characterization of nanostructured electrode by Linear Sweep Voltammetry (LCV)

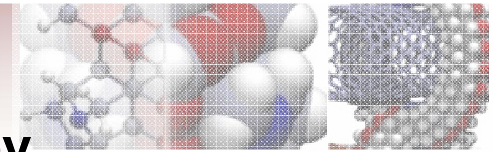


Oxidation of atenolol recorded by LCVs
Oxidation peak at ~ 0.6V/SCE



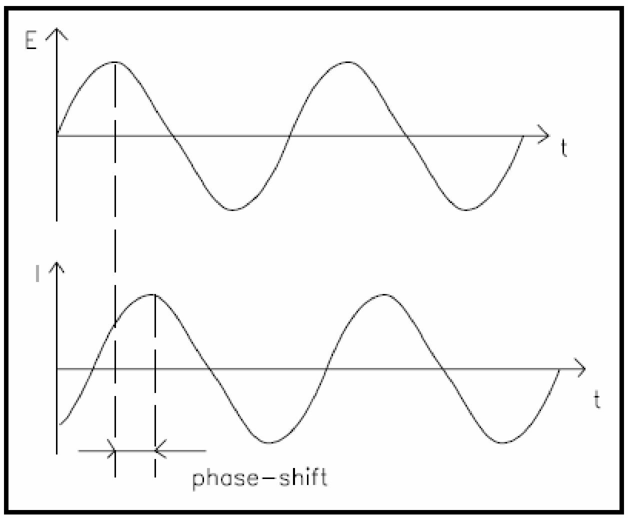
Oxidation of atenolol recorded by LCV, with unmodified electrode

Calibration curve for atenolol detection (detection limit 3.9 x 10^{-7} M)



Characterization of nanostructured electrode by Electrochemical Impedance Spectroscopy (EIS)

- electrochemical impedance is measured by applying a small AC potential to an electrochemical cell
- the response to this potential is an AC current signal
- this current signal can be analyzed as a sum of sinusoidal functions (a Fourier series)



Sinusoidal current response in a linear system

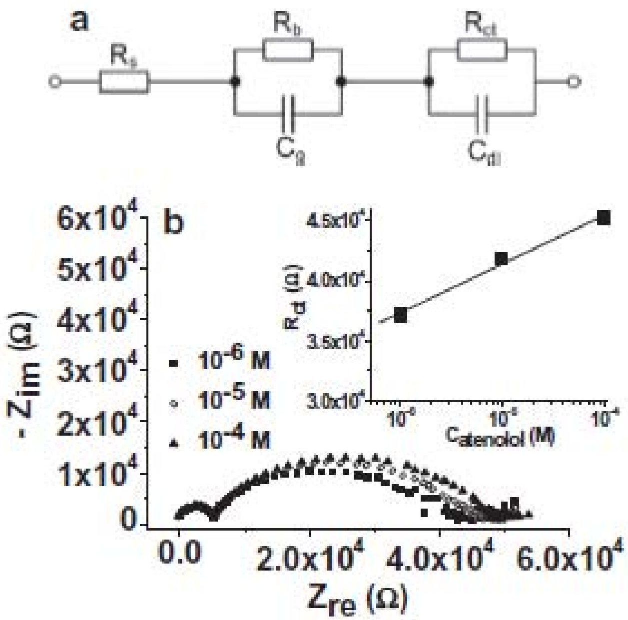
$$E_t = E_0 \sin(\omega t)$$ Excitation signal

$$I_t = I_0 \sin(\omega t + \phi)$$ Response signal

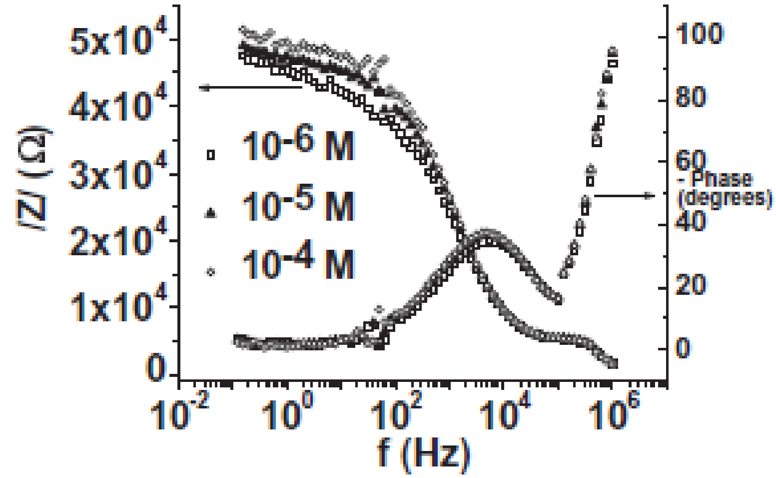
$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$ Impedance of the system

Frequency range: 0.01- 10^6 Hz

Excitation signal = 10 mV



Nyquist diagrams obtained at various concentration of atenolol
Inset: variation of charge-transfer resistance with atenolol concentration



Bode diagrams obtained at various concentration of atenolol (10^{-6} – 10^{-4} M) in Britton-Robinson buffer

$$Z_{tot} = R_S + \frac{R_b}{1+\omega^2 C_g^2 R_b^2} + \frac{R_{ct}}{1+\omega^2 C_{dl}^2 R_{ct}^2} - j\left(\frac{\omega C_g R_b^2}{1+\omega^2 C_g^2 R_b^2} + \frac{\omega C_{dl} R_{ct}^2}{1+\omega^2 C_{dl}^2 R_{ct}^2}\right)$$

$$Z_{re} = R_S + \frac{R_b}{1+\omega^2 C_g^2 R_b^2} + \frac{R_{ct}}{1+\omega^2 C_{dl}^2 R_{ct}^2}$$

$$Z_{im} = \frac{\omega C_g R_b^2}{1+\omega^2 C_g^2 R_b^2} + \frac{\omega C_{dl} R_{ct}^2}{1+\omega^2 C_{dl}^2 R_{ct}^2}$$

$$|Z| = \sqrt{(Z_{re})^2 + (Z_{im})^2}$$

CONCLUSIONS

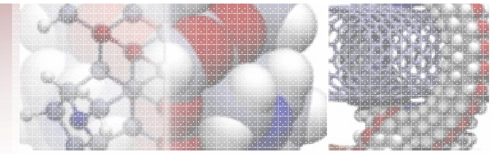
- Metallic nanoparticles linked to DNA can be successfully applied in microelectronics as nano-connectors
- Metallic nanoparticles linked to electrode surface greatly enhanced its electrocatalytic activity

Future work

Graphene-metal nanoparticles based electrodes for detection of pharmaceutical pollutants

Carbon nanotube based electrodes for studying DNA oxidation

Usage of amino acid capped nanoparticles in medicine



Papers (2009-2011)

1. Pruneanu, S; Pogacean, F; Grosan, C, et al., **CHEMICAL PHYSICS LETTERS** Volume: **504** Issue: **1-3** Pages: **56-61, 2011**

2. Vlascici, D; Pruneanu, S; Olenic, L, et al. **SENSORS** Volume: 10 Issue: 10 Pages: 8850-8864, 2010

3. Orza, A; Olenic, L; Pruneanu, S, et al. **CHEMICAL PHYSICS** Volume: 373 Issue: 3 Pages: 295-299, 2010

4. Balasoiu, SC; Stefan-van Staden, RI; van Staden, JF, et al. **ANALYTICA CHIMICA ACTA** Volume: 668 Issue: 2 Pages: 201-207, 2010

5. Pruneanu, S; Olenic, L; Al-Said, SAF, et al. **JOURNAL OF MATERIALS SCIENCE** Volume: 45 Issue: 12 Pages: 3151-3159 2010

6. Al-Said, SAF; Hassanien, R; Hannant, J, et al. **ELECTROCHEMISTRY COMMUNICATIONS** Volume: 11 Issue: 3 Pages: 550-553, 2009

7. Olenic, L; Mihailescu, G; Pruneanu, S, et al. **JOURNAL OF MATERIALS SCIENCE-MATERIALS IN MEDICINE** Volume: 20 Issue: 1 Pages: 177-183, 2009

8. Henderson, AP; Seetohul, LN; Dean, AK, et al., **LANGMUIR** Volume: 25 Issue: 2 Pages: 931-938 Published: 2009

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