Project title:

Advanced piezoelectric materials functionalized for the quality and security control of food

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Magyarország-Románia Határon Átnyúló Együttműködési Program 2007-2013

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Objectives of the research program:

1., General consideration regarding biosensitive devices:

General considerations regarding synthesis methods for achievement of new piezoelectric materials, their characterization (structural analysis and physical properties) methods, sensors achievement (Uni. of Bucharest), functionalizing and testing methods and different design types for bio-sensitive devices (Uni. of Szeged).

2., Achievement and characterization of piezoelectric materials. Biosensitive devices design:

Hydrotermal synthesis (Uni. of Bucharest), characterization and piezoelectric parameters determination of piezoelectric materials, bio-sensitive devices design (Uni. of Szeged).

3., Manufacture, functionalizing and testing of sensors. Elaboration of comparative studies. Manufacture of biosensitive devices:

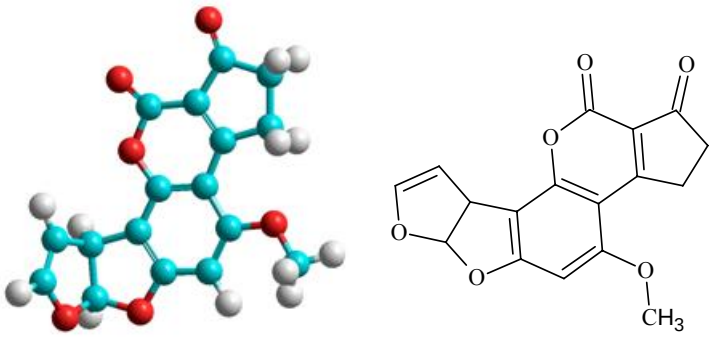
Manufacture of sensors, their functionalizing and testing, elaboration of comparative studies and manufacture of biosensitive devices (Uni. of Szeged and Bucharest) .

4., Process, materials and devices optimization:

Optimization of the synthesis methods, piezoelectric materials and bio-sensitive devices, efficiency increasing (Uni. of Szeged and Bucharest).

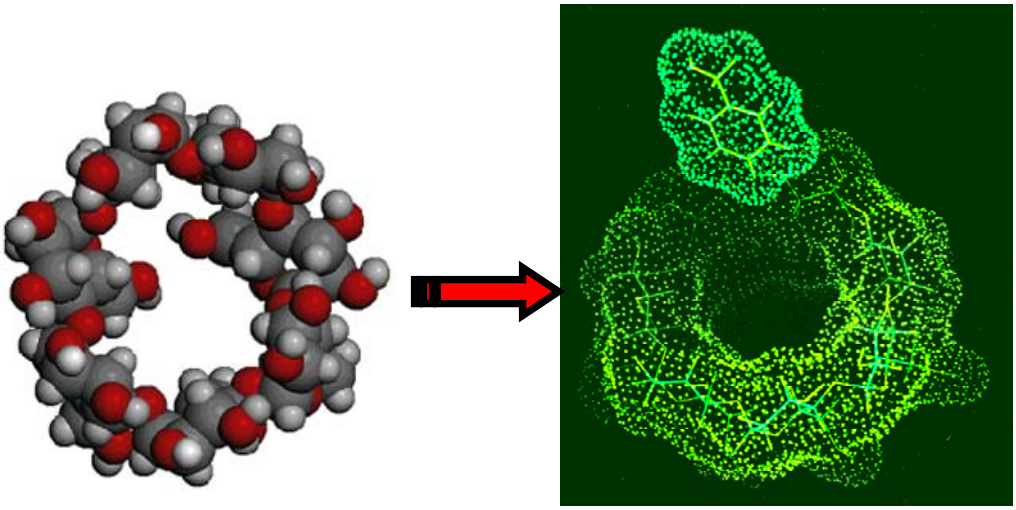
Summary of our results:

The aim of this work are developing a new selective sensor to detection of aflatoxins. Aflatoxins are carciogenic and harmful for gene and occur in nature. The B1 molecule (1. Fig.) is the most efficient impurities in foods.

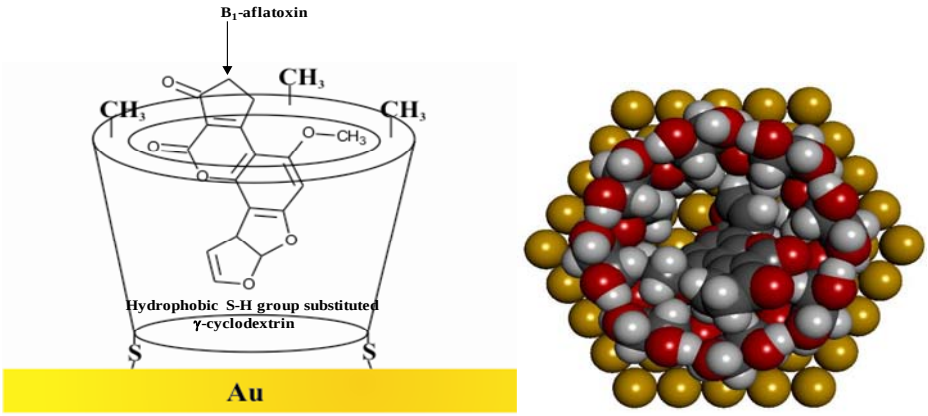


1. Fig. Aflatoxin B1 molecules.

It is present generally in imports. Our clime is more and more warm and wet with gradual changes in the clime, so the toxin producing funguses will be exceed in number. It can be very interesting to detect this toxin with selective sensors. We use functionalised gold nanoparticles and gold nanofilms to build up sensors. The functionalisation of surface can be prepared with cyclodextrines (2. Fig.) which are modified by thiol or fluorescent group.

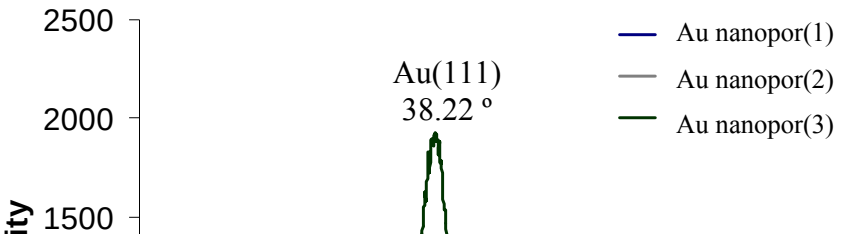


2. Fig. Cyclodextrin molecules (left side: 3D structure) and a complex (right side).



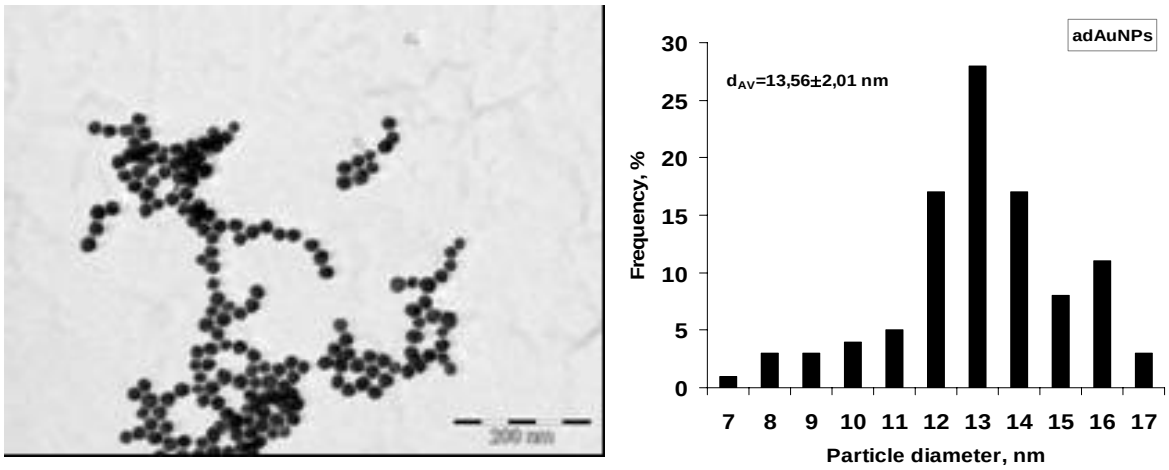
3. Fig. Aflatoxin B1 dockage to a thiol modified γ-cyclodextrin molecules (left side), and a γ-cyclodextrin on gold surface (111) optimalized by PM6-DH+ method.

We prepared citrate and aminodextran reduced gold nanoparticles to preparation gold nanofilms. Identification and characterization of gold nanoparticles were performed by their XRD diffratogramms (4. Fig.),



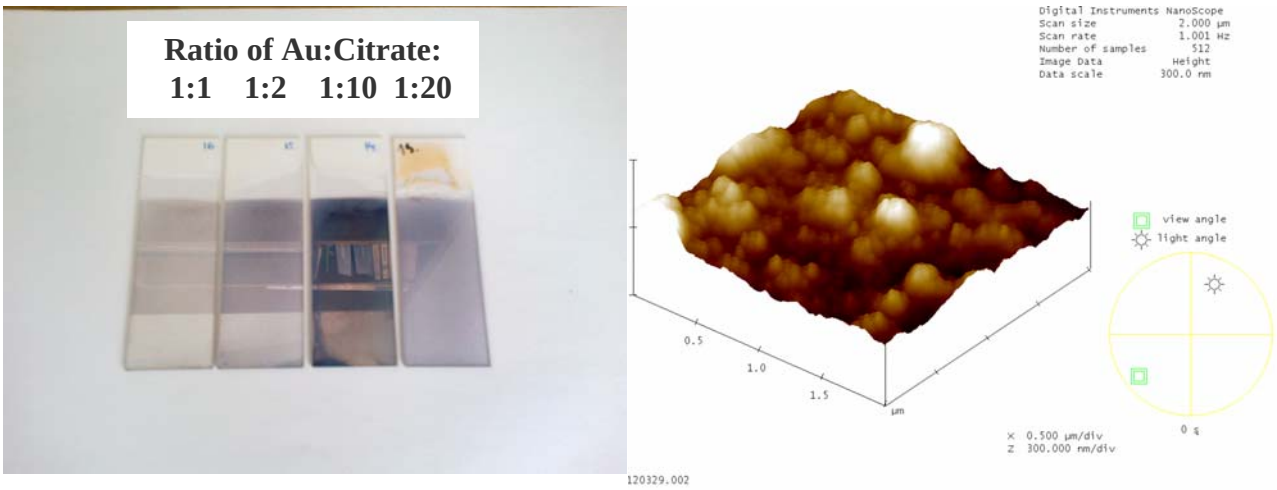
4. Fig. Diffraktograms of gold nanoparticles.

UV-Vis spectras and TEM images. These methods showed the avarege diameters of gold nanoparticles were 13,5 nm (aminodextran reduced, 5. Fig.) and 10,3 nm (citrate reduced), and the distribution are homogenous.



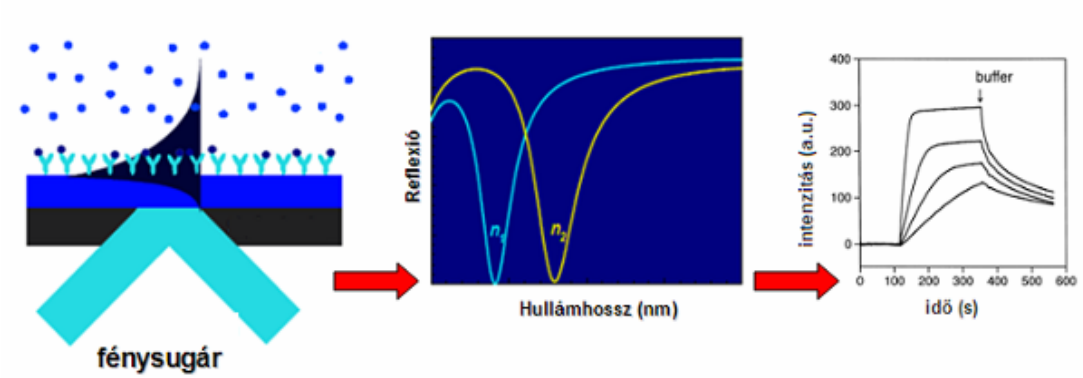
5. Fig. TEM images of aminodextran reduced AuNPs ($c_{Au}=5*10^{-4}$M).

The surface plasmon resonance were 517 and 528 nm (aminodextran and citrate reduced in order). We can be established uniform conductor films on silica crystal and glass surfaces (6. Fig.) by spray-coating technology from the prepared gold nanosols if the SiO_2 surfaces were treated previous by PEI (positive charged layer). These specifically produced films may be suitable in biosensors.



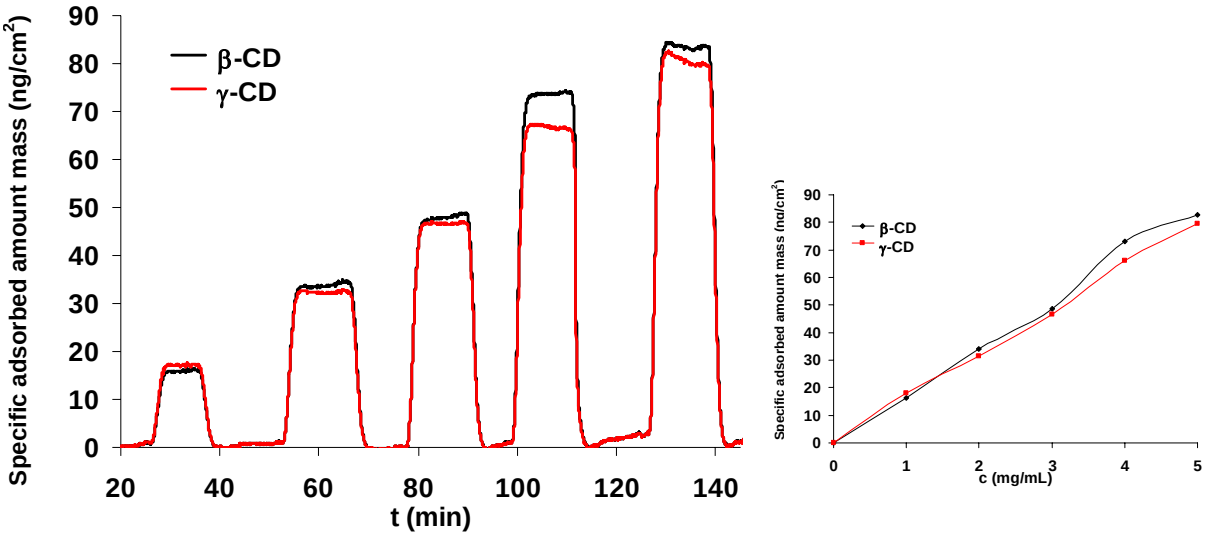
6. Fig. Photos about citrate reduced gold nanofilms on SiO_2 surfaces and AFM image of 5 layers film .

The maximum absorbed amount of β– and γ–CD (cyclodextrin) on gold surfaces were determined from SPR (7. and 8. Fig.) and QCM measurments (10. Fig.).



7. Fig. Shematic reprezentation of functional disciple of Surface plasmon resonance.

8. Fig. Plasmon II. SPR set (the resolution of set is 2.5 x 10^{-8} refraction coefficient unit).



9. Fig. Absorbed amount of cyclodextrins.

These were 80 ng/cm^2 from SPR results and the binding was physisorption. We have modelled in QCM measurements the surface which was prepared to spray-coating.

10. Fig. SRS QCM200 set and SRS QCM200 crystals (gold, silver, cooper or rather platinum coating).

First the gold surfaces were treated by PEI after gold nanoparticles and then was measured the attaching of cyclodextrins. The absorbed amount of PEI was 185 ng/cm^2 while the amount of gold was 150 ng/cm^2. Cyclodextrins attached by physisorption as expected like SPR measurements and unlike thiol groups modified cyclodextrins.

Fluorescence measurements of cyclodextrins and gold nanosols showed that the extictions and emissions peak of γ- and β-CD appeared on 390 and 450 nm. The aminodextran reduced gold nanoparticles decreased the intensitity of fluorescence. Increased the concentration of Au nanoparticles (0,042- 0,208 mM) intensified the decreasing.

Furthermore it will be studied attaching of aflatoxin molecules to cyclodextrin modified gold surface by SPR and QCM measurements.
For comparison it will be performed quantitative analysis of aflatoxin molecules on surfaces modified gold nanoparticles by ELISA (Enzyme-Linked ImmunoSorbent Assay) method.
Validation of thiol modified gold nanosensors on silica cristal will be performed by HPLC-MS method. Limit value of aflatoxins in various foodstoffs:

Foodstuffs ([1])		Maximum levels (µg/kg)		
2.1.	Aflatoxins	B1	Sum of B1, B2, G1 and G2	M1
2.1.1.	Groundnuts to be subjected to sorting, or other physical treatment, before human consumption or use as an ingredient in foodstuffs	8.0 ([5])	15.0 ([5])	-
2.1.2.	Nuts to be subjected to sorting, or other physical treatment, before human consumption or use as an ingredient in foodstuffs	5.0 ([5])	10.0 ([5])	-
2.1.3.	Groundnuts and nuts and processed products thereof, intended for direct human consumption or use as an ingredient in foodstuffs	2.0 ([5])	4.0 ([5])	-
2.1.4.	Dried fruit to be subjected to sorting, or other physical treatment, before human consumption or use as an ingredient in foodstuffs	5.0	10.0	-
2.1.5.	Dried fruit and processed products thereof, intended for direct human consumption or use as an ingredient in foodstuffs	2.0	4.0	-
2.1.6.	All cereals and all products derived from cereals, including processed cereal products, with the exception of foodstuffs listed in 2.1.7., 2.1.10. and 2.1.12.	2.0	4.0	-
2.1.7.	Maize to be subjected to sorting or other physical treatment before human consumption or use as an ingredient in foodstuffs	5.0	10.0	-
2.1.8.	Raw milk ([6]), heat-treated milk and milk for the manufacture of milk-based products	-	-	0.050
2.1.9.	Following species of spices: Capsicum spp. (dried fruits thereof, whole or ground, including chillies, chilli powder, cayenne and paprika) Piper spp. (fruits thereof, including white and black pepper) Myristica fragrans (nutmeg) Zingiber officinale (ginger) Curcuma longa (turmeric)	5.0	10.0	-
2.1.10.	Processed cereal-based foods and baby foods for infants and young children ([3]) ([7])	0.1	-	-
2.1.11.	Infant formulae and follow-on formulae, including infant milk and follow-on milk ([4]) ([8])	-	-	0.025
2.1.12.	Dietary foods for special medical purposes ([9]) ([10]) intended specifically for infants	0.1	-	0.025

11. Fig. „ERANET Group” in Szeged.
Prof. Dr. Imre Dékány, full professor, Judit Szalmáné Ménesi, dipl. Chemist, Istvánné Polgár, technical assistant