

Plasmonic nanostructures employed for optical and colorimetric (bio)sensing strategies

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"any intentionally produced material that has one or more dimensions of the order of 100 nm or less

or that is composed of discrete functional parts, either internally or at the surface, many of which have one or more dimensions of the order of 100 nm or less, including structures, agglomerates or aggregates, which may have a size above the order of 100 nm but retain properties that are characteristic of the nanoscale".



Regulation (EU) 2015/2283 of the European Parliament and of the Council of 25 November 2015 on novel foods, amending Regulation (EU) No 1169/2011 of the European Parliament and of the Council and repealing Regulation (EC) No 258/97 of the European Parliament and of the Council and Commission Regulation (EC) No 1852/2001 (Text with EEA relevance)

Is this Nano?

AC

GROWING THE CAPABILITIES OF



2015 2016

2017

Year



European Commission, Commission Recommendation of 18 October 2011 on the definition of nanomaterial, Official Journal of the European Union. 2011/696/EU: 38-40, 2011

SENSOR* AND NANO*

SORBENT* AND NANO*

N&N



Nanomaterials



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Metal based Nanoparticles





Metal based Nanoparticles





Advantages of metal nanoparticles for analyitical purposes



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Metal Nanoparticles application fields





Nanoparticles in analytical chemistry and food analysis





Plasmonic-active nanostructured materials for sensing and biosensing

Surface plasmon resonance (SPR) is a phenomenon where the electrons in the metal surface layer are excited by photons of incident light with a certain angle of incidence, and then propagate parallel to the metal surface (Zeng et al., 2017)



Electromagnetic/Evanescent wave



MNPs and (L)SPR





Figure 1. A) Prism coupling configuration of SPR, where a light beam impinges on a thin metallic film deposited on a prism. P-polarized light absorbed by the surface plasmon is seen from a minimum in the reflection spectra. B) Representation of the localized surface plasmon on nanoparticles and absorbance spectra obtained for binding events on nanoparticles.

MNPs and (L)SPR

Metal nanoparticles

From Romans...

Nanotecnologia romana

I colori cangianti della Coppa di Licurgo, datata IV secolo a.C., sono dovuti a nanoparticelle di oro e argento disperse nella matrice vetrosa.

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D. A., Zhang, Y., Dubonos, S. V., ... & Firsov, A. A. (2004). science, 306(5696), 666-669.

Localized Surface Plasmon Resonance (LSPR)

Localized Surface Plasmon Resonance (LSPR)

MNPs and LSPR

Metal nanoparticles: their camaleontic features

MNPs can interact in different ways with VIS-electromagnetic radiation depending on their shapes, sizes, and composition.

Gold nanoparticles

10 nm

Gold nanorods

Silica-gold core-shell nanoparticles

Nanoshells

Gold nanocages

Nanocages

50 nm

MNPs and LSPR

Metal nanoparticles: their camaleontic features

Plasmonic-active nanostructured materials for sensing and biosensing

Colloidal metal nanoparticles based assays

Renediktas Brasiunas 🛱 Anton Ponov 🛱 Anunas Ramanavicius 🛱 Almira Ramanaviciene 🎗 🛱

Localized Surface Plasmon Resonance

20019 A

Plasmonic-active nanostructured materials for sensing and biosensing

Main pillar

Concentration

Sintesi nanoparticelle

Sintesi generica con riduzione del precursore metallico

3. coalescence of clusters and nanoparticles

Main strategy

Analytical signal

Phenolic content and antioxidant capacity evaluation trough Au and AgNPs formation

Antioxidant Capacity

Class Selective

C AuNPs

λ (nm)

Total phenolic content

Phenolic content and antioxidant capacity evaluation trough Au and AgNPs formation

Fig. 2. PCA of the ABTS, FC, AuNPs and the proposed AgNPs-based methods reactivity vs. polyphenolic compounds. The biplot (Score and loading) of the first two principal components showed 82.85% of the cumulative variance. Rows normalization were applied to the dataset. Data were autoscaled before PCA.

R	ABTS	FC	AgNPs-HT	AgNPs-RT	AuNPs
ABTS	1	0.876	0.891	0.956	0.977
FC	0.876	1	0.733	0.913	0.801
AgNPs-HT	0.891	0.733	1	0.770	0.826
AgNPs-RT	0.956	0.913	0.770	1	0.950
AuNPs	0.977	0.801	0.826	0.950	1

VT: Vanilla Tea
TG: Green Tea
TC: Classic Tea
SD: sogni d'oro infused
RE: Relax infused
RB: Rosa di bosco Infused
LT: Lemon Tea
IN: Finocchio infused
DIG: Digestiva infused

Sugars content evaluation trough AgNPs formation

Ion chromatography Sample AgNPs assay RSD RSD **Rel. error** $(g 100 \text{ mL}^{-1}, \text{Glu}, \text{Eq.})$ (%, n = 5) $(g 100 \text{ mL}^{-1}, \text{Glu} + \text{Fru})$ (%, n = 3) (%) Peach tea 2.98 ± 0.14 4.74 2.71 +5.0 3.13 ± 0.08 Black tea 3.56 ± 0.23 6.51 3.05 ± 0.11 3.56 - 14.3 Coconut water 4.72 ± 0.13 2.84 4.93 ± 0.05 0.98 +4.4 3.50 ± 0.25 7.23 3.53 ± 0.04 1.21 Gaseous +0.9Cedrata 9.36 ± 0.27 8.9 2.85 8.74 ± 0.78 - 6.6 6.11 ± 0.07 Tonic water 1.15 5.62 ± 0.12 2.11- 8.0 Apple 1 1.67 ± 0.02 1.12 1.50 ± 0.02 1.11 - 10.2 Apple 2 1.78 0.0 1.14 ± 0.04 3.41 1.14 ± 0.02 Apple 3 3.27 ± 0.04 1.30 3.12 ± 0.10 3.10 - 4.6 Apple 4 2.43 ± 0.23 9.42 2.67 ± 0.11 4.10 +9.9Apple 5 2.43 ± 0.02 0.74 2.31 ± 0.9 3.80 - 5.0

Recovery: 86-118%

 $R^2 \ge 0.991$ Monosaccharides and polyols LOD= $8.7 \pm 0.4 \mu M$ Disaccharides average LOD= $120 \pm 0.1 \mu M$ RSD $\le 8\%$

AgNPs Morphological study

SURFACE FUNCTIONALIZATION!!!

AgNPs Morphological study

TEM

DLS

6

4

2

0

0

5

10

15

20

AgNPs size (d, nm)

25

30

35

40

SURFACE FUNCTIONALIZATION!!!

Glucose

Intensity (%)

Sucrose

Xylitol

100 nm

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Colorimetric detection of sugars based on gold nanoparticle formation Gerardo Palazzoª, Laura Facchiniª, Antonia Mallardi^{b,*}

STRATEGY 1

The "pink assay" is based on the sugar assisted chemical synthesis of NPs and it represents a simple one-step colorimetric approach to the quantification of all potentially reducing sugars (sucrose included) with a LOD of 10 M.

Sugars sensing

1.4 -

1.2

1.0

0.8

0.6

0.4

0.2

Absorbance

Α

в

1.5

1.0

0.5

at 530 nm

Absorbance

1.50 mM

1.00 mM

0.60 mM

0.36 mM

0.24 mM

0.12 mM

0.06 mM 0.03 mM

0 mM

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Sugars content evaluation trough AuNPs formation

Colorimetric detection of sugars based on gold nanoparticle formation Gerardo Palazzo^a, Laura Facchini^a, Antonia Mallardi^{b,*}

STRATEGY 2

The "blue assay" is based on the Au-NP synthesis catalysed by the enzyme glucose oxidase and it is specific for glucose, with a LOD of 5 M.

This enzyme catalyses the **glucose oxidation** to gluconic acid **by a final electron acceptor**, **usually molecular oxygen**. Recently, the ability of glucose oxidase to reduce, in presence of glucose, Au³⁺ ions to Au⁰ has been reported and proposed as a route to the synthesis of Au-NPs of controlled size. Here we exploit this reaction to selectively quantify the glucose. Au-NP synthesis was achieved by adding the enzyme GOD to a buffered solution (pH = 7.0) of HAuCl₄ and glucose, and incubating at 37 °C for 90 min. Blue NPs (see picture) were **obtained while the reaction does not take place in absence of glucose or glucose oxidase**.

Metal nanoparticle-based seed-growth strategies

Main strategy

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Reducing sugars monitoring trough AgNPs growth

Studies on Silver Nanoparticles Production Mediated by Sugars

Annalisa Scroccarello, Flavio Della Pelle, Simona Scarano

G. Di Francia et al. (eds.), Sensors and Microsystems, Lecture Notes in Electrical Engineering 629, https://doi.org/10.1007/978-3-030-37558-4_5

Xylitol monitoring trough AuNPs growth

Seed formation and growth phenomena study

The early nucleation stage of gold nanoparticles formation in solution as powerful tool for the colorimetric determination of reducing agents: The case of xylitol and total polyols in oral fluid

Dose-response kinetic and curve

Xylitol monitoring in human saliva trough AuNPs growth

Recovery study

Xylitol montoring along 1 hours of chewin-gum mastication

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Metal nanoparticle etching


Main strategy



Analytical signal











Etching



H₂O₂ determination trough MNPs etching



A self-referenced optical colorimetric sensor based on silver and gold nanoparticles for quantitative determination of hydrogen peroxide

CrossMark

Pedro J. Rivero^{a,*}, Elia Ibañez^b, Javier Goicoechea^b, Aitor Urrutia^b, Ignacio R. Matias^c, Francisco J. Arregui^b



Etching phenomena study





Etching phenomena study. H₂O₂ determination





Glucose and cholesterol evaluation trough MNPs etching



Xuehong Zhang,^a Min Wei,^b Bingjing Lv,^a Yuanjian Liu,^a Xu Liu^a and Wei Wei^{*a}

Sensitive colorimetric detection of glucose and

cholesterol by using Au@Ag core-shell

nanoparticles*

CrossMark

Cite this: RSC Adv., 2016, 6, 35001

its application for the colorimetric detection of H_2O_2 and glucose/ cholesterol.



23.8

0.55

0

27.2

10 20 30 40 50 Ni²⁺Conc. (nM)

30.6

Nickel determination











Main strategy



Main strategy



Analytical signal



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Main strategy







Immuno-based determination of HIgG





Naked

40 nm

40 nm

40 nm

40 nr

80 nm

40 nn

Marzia Iarossi,^{†,||} Chiara Schiattarella,^{†,‡} Ilaria Rea,[‡] Luca De Stefano,[‡] Rosalba Fittipaldi,[§] Antonio Vecchione,[§] Raffaele Velotta,^{*,†}[©] and Bartolomeo Della Ventura[†]

Functionalized Gold Nanoparticles

Cite This: ACS Omega 2018, 3, 3805-3812

Colorimetric Immunosensor by Aggregation of Photochemically

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Cd²⁺ indirect determination trough AuNPs aggregation



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Cd²⁺ indirect determination assay format



Fig. 2. Detection process of smartphone based colorimetric reader system.

Cd²⁺ indirect determination

Dose-response curve



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Recovery study

	Determination of Cd ²⁺	in tap	water	samples	using	the	proposed	method.
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Samples	Spiked concentration (µg/L)	This colorimetric system		Microplate reader	
		Determined conc. (µg/L)	Recovery%	Determined conc. (µg/L)	Recovery%
1	5	5.18	116.4	5.21	104.3
2	10	11.32	113.2	10.96	109.6
3	10	11.61	116.1	10.83	108.3
4	20	21.63	108.15	20.12	100.6
5	20	23.56	117.8	22.15	110.8

Colorimetric approach



From plasmonic... Towards colorimetric strategies





Optical spectroscopic methods/ Spectrochemical methods. WHICH COLOR I PERCEIVE?

The Visible Spectrum					
Wavelength Region	Color of Light	Complementary Color			
Absorbed, nm	Absorbed	Transmitted			
400–435	Violet	Yellow-green			
435–480	Blue	Yellow			
480–490	Blue-green	Orange			
490–500	Green-blue	Red			
500–560	Green	Purple			
560–580	Yellow-green	Violet			
580–595	Yellow	Blue			
595–650	Orange	Blue-green			
650–750	Red	Green-blue			

COLORIMETRY PILLAR



RGB COLORIMETRIC SPACE



COLORIMETRY PILLAR





Metal nanoparticles integration onto solid substrates







Paper as substrate



Paper as elective substrate





Fig. 1 Existing paper modification approaches for paper-based POCT. Different paper materials, including Fusion 5, filter paper, chromatography paper, cellulose paper, Whatman® No.1 filter paper and NC membrane, have been modified with various reagents for paper-based sample pretreatment and paper-based detection

Paper as elective substrate





MNPs as colorimetric probe

Analytica Chimica Acta 1183 (2021) 338971



Metal nanoparticles based lab-on-paper for phenolic compounds evaluation with no sample pretreatment. Application to extra virgin olive oil samples

Check for updates

Annalisa Scroccarello ^a, Flavio Della Pelle ^{a, *}, Daniel Rojas ^a, Giovanni Ferraro ^b, Emiliano Fratini ^b, Sara Gaggiotti ^c, Angelo Cichelli ^c, Dario Compagnone ^{a, **}

Office grade instruments



Thermal-roll laminator





MNPs as colorimetric probe: Device conceptualization and realization



MNPs as colorimetric probe: Extraction-free phenolic compounds determination

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Extraction-free olive oil phenolic compounds evaluation through a MNPs seed growth strategy



Extraction-free olive oil phenolic compounds evaluation trough a seed growth strategy

Dose-response curve



EVOO samples' phenolyc compounds content







Sample analysis, analytical performances



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No interterferences by compounds commonly present in EVOO

Low

Mean

High

Pesticides determination trough MNPs aggregation integrated in a paper-based device



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DI TERAMO

A paper-based colorimetric sensor array for discrimination and simultaneous determination of organophosphate and carbamate pesticides in tap water, apple juice, and rice

Top view

Side view

Microchimica Acta (2020) 187:621 https://doi.org/10.1007/s00604-020-04596-> ORIGINAL PAPER



Pesticides determination trough MNPs aggregation integrated in a paper-based device

Analytes screening









Paraoxon



Parathion







Chlorpyrifts

Diazinon



Malathion

Carbaryl



Malathion

Paraoxon

Diazinon



Chlorpyrifos

Parathion

Dose-response curve and analytical parameters



Carbaryl Paraoxon Parathion Malathion Diazinon Chlorpyrifos

H₂O₂ determination trough MNPs etching integrated in a paper-based substrate



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Arti



Development of a surface-modified paper-based colorimetric sensor using synthesized Ag NPs-alginate composite

Lokesh Sharma, Shubhankar Gouraj, Pranit Raut & Chandrakant Tagad 📼 🗓

H₂O₂ determination trough MNPs etching integrated in a paper-based substrate



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Advantages of metal nanoparticles for analyitical purposes



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Advantages of metal nanoparticles for analyitical purposes



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Advantages of metal nanoparticles for analyitical purposes



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Nanotechnology





Nanomaterials / metal nanoparticles



Biological features



Nanomaterials / metal nanoparticles



Biological features




Biological features



Annalisa Scroccarello^{a,1}, Bernardo Molina-Hernández Junior^{a,1}, Flavio Della Pelle^{a, e}, Johnny Ciancetta ^a, Giovanni Ferraro ^b, Emiliano Fratini ^b, Luca Valbonetti ^a, Clemencia Chaves Copez a, *, Dario Compagnone

FL SEVIE

Aspergillus niger

Metal nanoparticles formation

sensors

Capacity in Food

Flavio Della Pelle 😳 and Dario Compagnone * 💿

Nanomaterial-Based Sensing and Biosensing of Phenolic Compounds and Related Antioxidant

Phenolic content and antioxidant capacity evaluation trough Au and AgNPs formation

!!!! LAB PRACTICAL !!!

... Nanomaterial-based method for estimating the antioxidant activity relies on the polyphenol-mediated growth of MNPs (AuNPs and AgNPs), and optical monitoring of the corresponding plasmon absorption bands...

MDPI





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Biological features

Hyphae interaction

Control



AgNP@CT 15 ppm



HYPOTHESIS: - AgNPs adhesion - Membrane damages - Hyphae necrosis



Live and death kit assay





Evans blue assay

Control



Nanoparticles application in food technology





Commercial low-density polyethylene (LDPE) films coated using a layer-by-layer (LbL) technique by alternating the deposition of polyethyleneimine (PEI), poly(acrylic acid) polymer (PAA) solutions and antimicrobial silver nanoparticles (Ag).





The colour changes of a) LDPE films and b) LDPE LbL coated (3 coatings) films without Ag and c) AgNPs presence on LDPE LbL coated (3 coatings) films immersed in 0.5% AgNO₃, or d) AgNPs presence on LDPE LbL coated with (3 coatings) film immersed in 5% AgNO₃ and UV/ozone treated for 20 min.



(d) LbL coated (3 coating) immersed in 0,5% AgNO₃, (e) LbL coated (3 coatings) immersed in 2% AgNO₃; and (f) LbL coated (3 coatings) immersed in 5% AgNO₃. Scale bar = 500nm

		Inibition zone (mm²)	
	Film	S. aureus	P. fluorescens
	LPDE films	0.00	0.00
	LPDE + PEI/PAA (MpH)	350.4 ± 13.30	694.8 ± 19.15
	LPDE + PEI/PAA (NMpH)	460.0 ± 25.41	737.0 ± 15.08



Biological features





Optical/ biological features – Imaging





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