

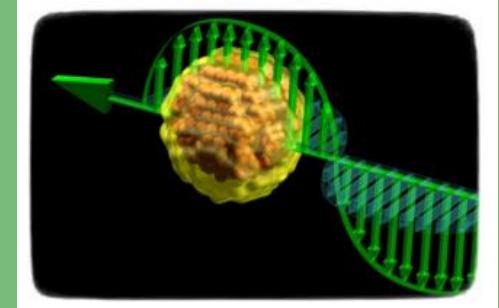
# Magneto-optics and Magneto-plasmonics

César de Julián Fernández



IMEM-CNR Parma

*Magnetic Materials Group*



Advanced magnetic materials and devices for biomedical applications  
Italian School of Magnetism  
Turin , 21-25 May 2018

## 1. Magneto-optics

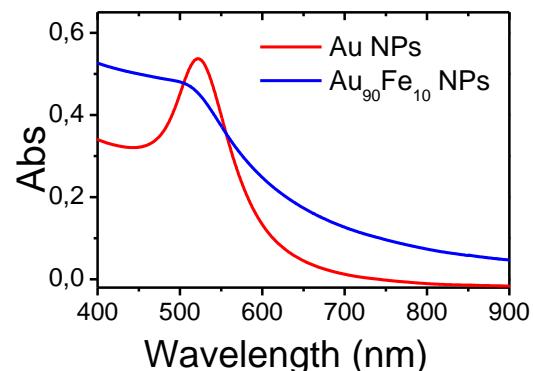
- a General phenomenology and materials
- b Applications of plasmonics in bio

## 2. Plasmonics

- a General phenomenology and materials
- b Applications of plasmonics in bio

## 3. Magnetoplasmonics

- a Plasmonics and magnetism?
- b Magnetoplasmonics materials and phenomena
- c Applications in bio



## Purpose of magnetoplasmonics (bio)



## Can support magnetic materials SPR?

$$\sigma_{\text{ext}} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}$$

	$\omega_p$ (eV)	$\varepsilon_1$ 633 nm	$\varepsilon_2$ 633 nm
Au	8.9	-11.7	1.26
Ag	9.2	-18.3	0.48
Co	9.74	-12.5	18.4
Fe	17.0	-1.03	17.6
Ni	9	-13.0	16.3

Nickel is the best!!!  
But always dumping

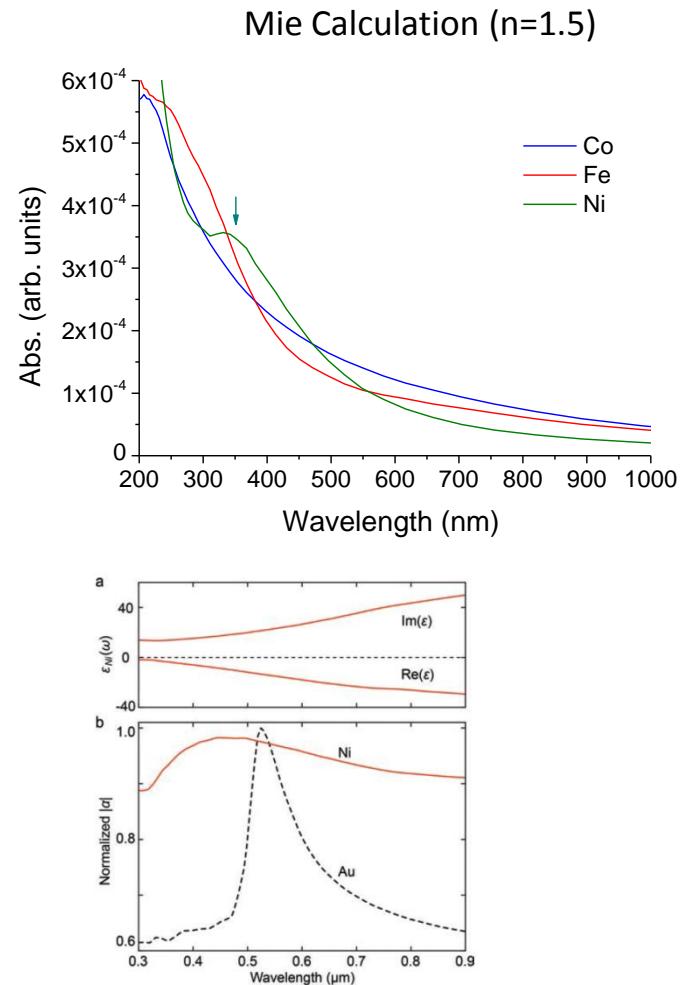


Figure 1. a) Dielectric function of nickel taken from Palik.<sup>[25]</sup>  
b) Comparison of the polarizability  $|\alpha|$  of nickel and gold spheres.

## Can support magnetic materials SPR?

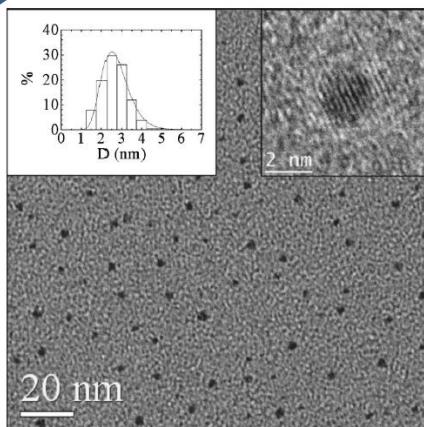
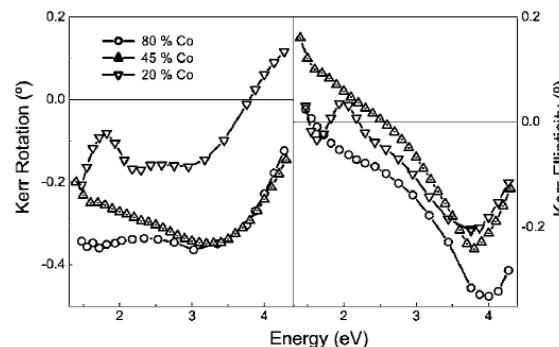
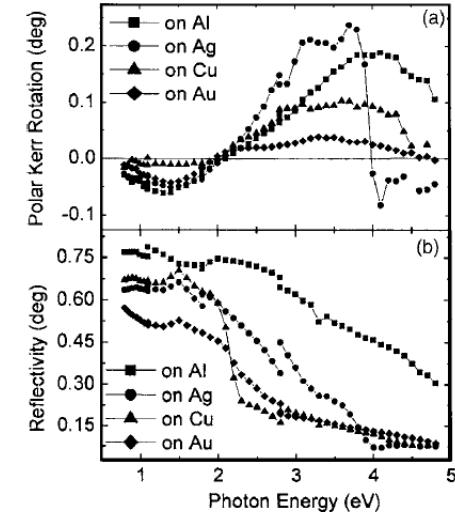


FIG. 1. TEM images of a Co-ZrO<sub>2</sub> granular film with 20% Co. Right-hand-side inset shows the magnification of one nanoparticle. Left-hand-side inset shows the histogram of the size distribution obtained from the TEM micrograph.

Co NPs



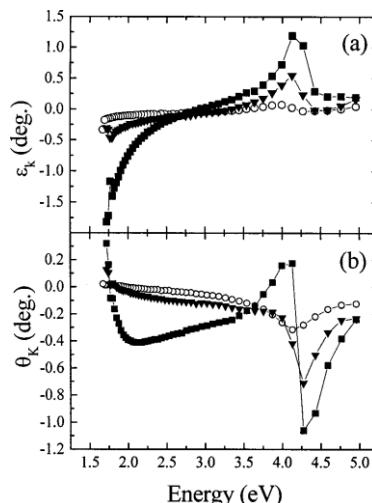
Clavero et al. J. Appl. Phys. 100, (2006) 074320



Kalska et al. J. Appl. Phys. 98 (2005) 44318

Fe NPs

Menendez et al.  
PRB 65, (2002) 205413

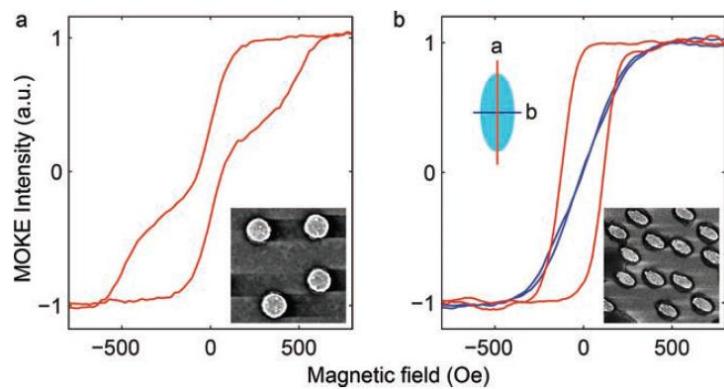


SPR in nUV

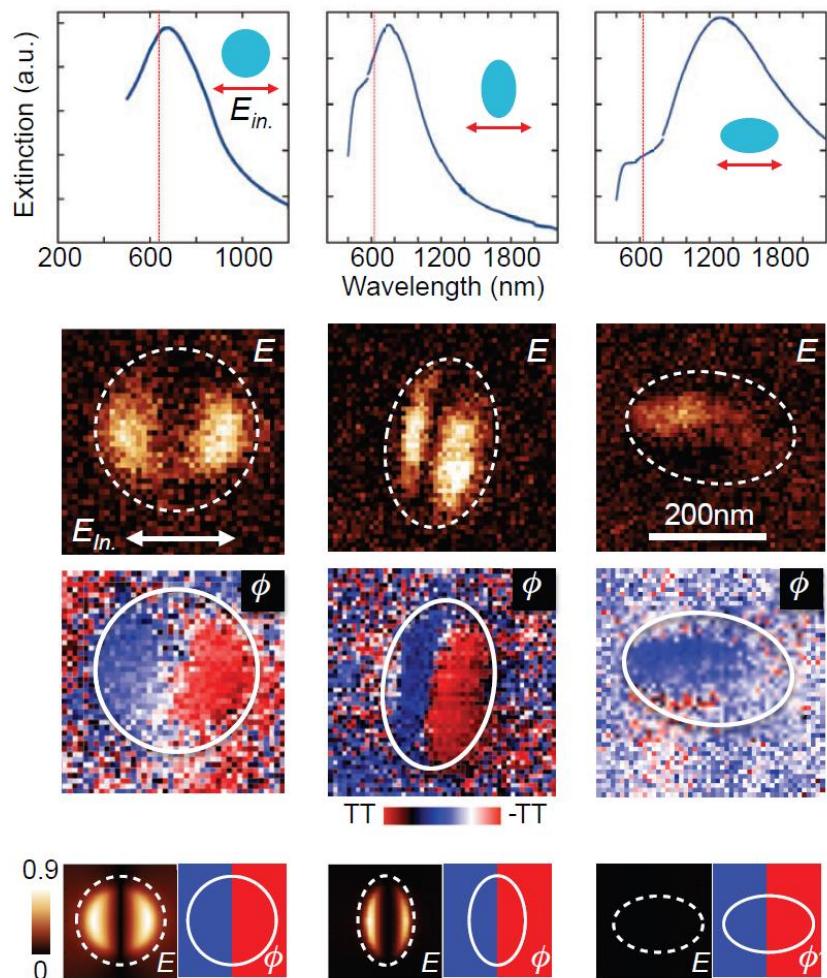
Mie model does not work  
Electronic structure of Nano Oxidation

## Can support magnetic materials SPR?

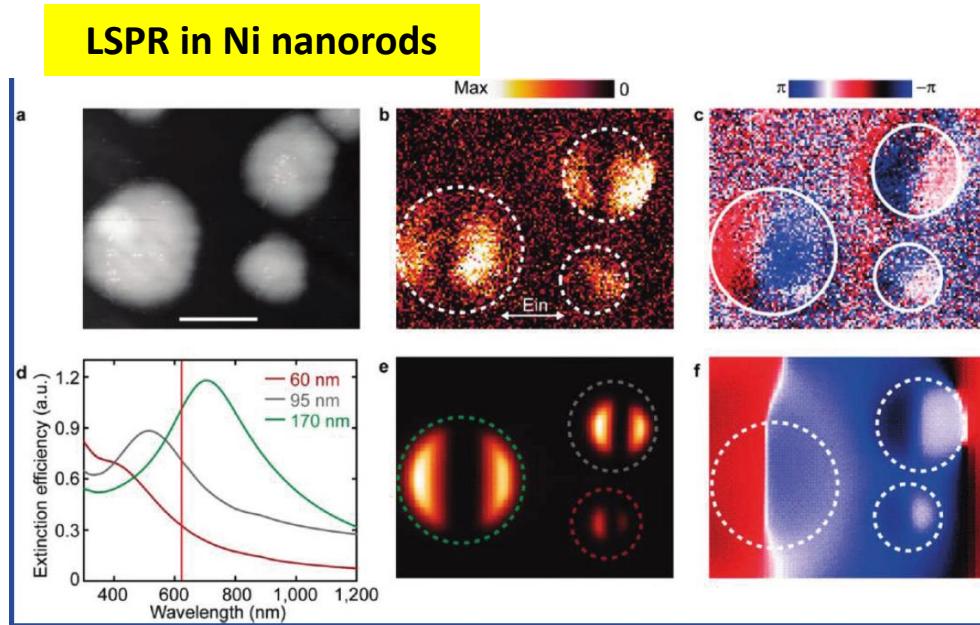
### LSPR in Ni nanorods



- Shape improves LSPR
- LSPR moves to IR
- Phase change allows observation of SPR

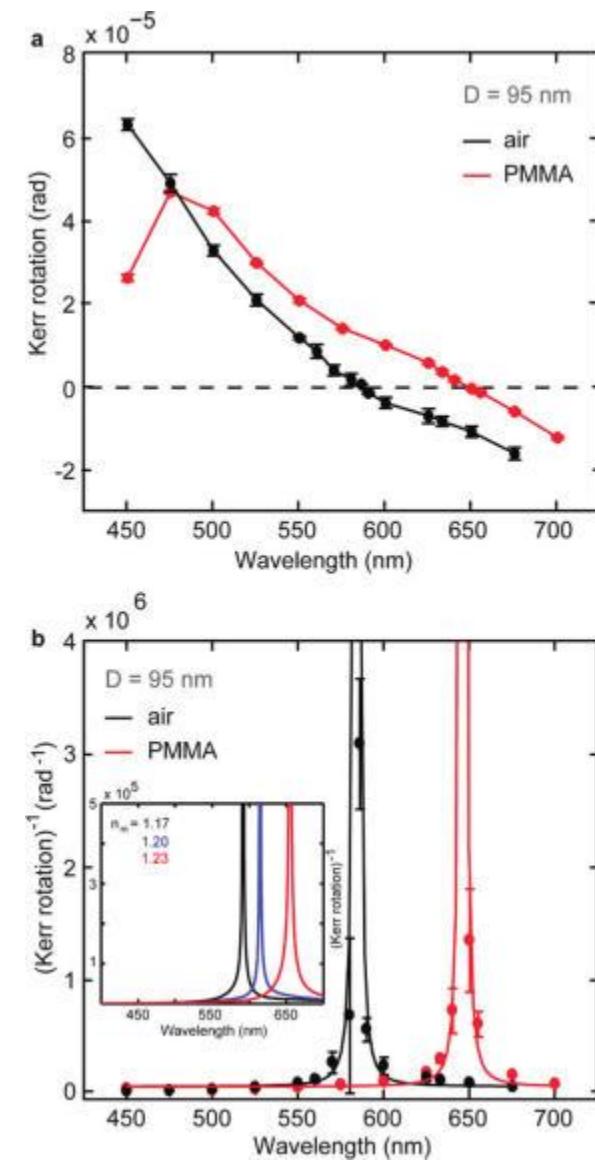


## Can support magnetic materials SPR?



MO at the SPR? Yes

- Change of sign of the MO Phase above and below the SPR
- Novel concept of sensing : Work with MOKE=0
- Tunability of MO-SPR with the magnetic field



## MO effects in Plasmonics materials? (non-magnetic conductors)

Yes

Faraday Effect

$$m \frac{d\vec{v}}{dt} + \gamma m \vec{v} = e\vec{E} + e\vec{v} \times \vec{B}$$

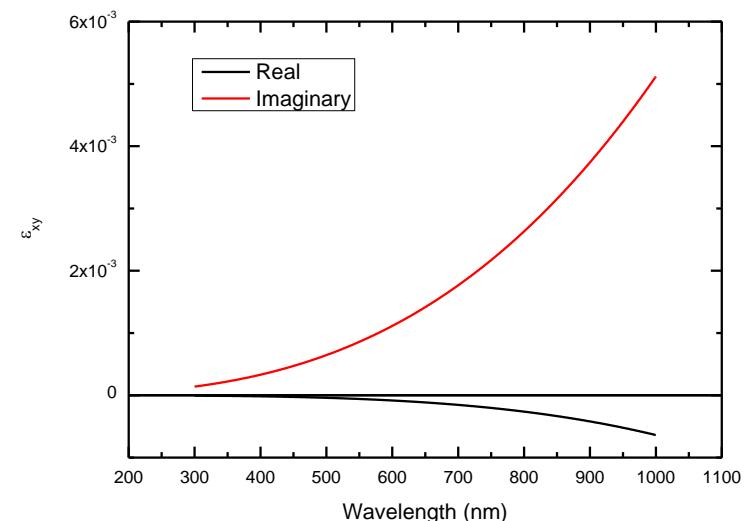
Drude model

Optical and MO properties

$$\epsilon_{xx} = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}$$

$$\epsilon_{xy} = i \frac{\omega_p^2 \omega_C}{\omega^2 + i\omega\gamma} \quad \omega_C = \frac{eB}{m}$$

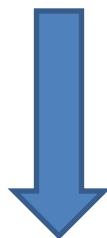
For Au (600 nm, B=1 T)  $\epsilon_{xy}=1.2 \cdot 10^{-4} + i1.5 \cdot 10^{-3}$



## MO effects in Plasmonics materials?

$$\alpha_0 = 3V \frac{\varepsilon - I}{\varepsilon + 2I}$$

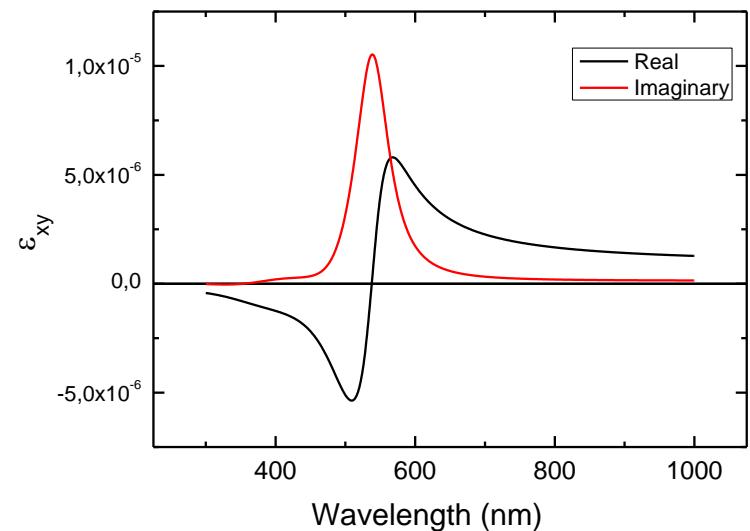
$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \varepsilon = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & 0 \\ -\varepsilon_{xy} & \varepsilon_{xx} & 0 \\ 0 & 0 & \varepsilon_{xx} \end{pmatrix}$$



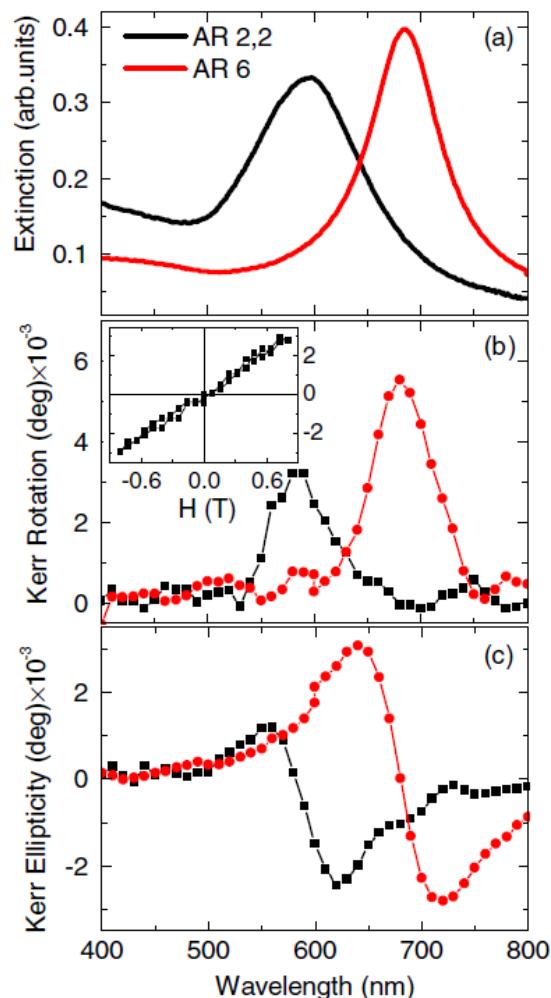
$$\psi = \theta_K + i\varepsilon_K = \frac{3\varepsilon_d\varepsilon_{xy}}{(\varepsilon_{xx}^r + i\varepsilon_{xx}^i - \varepsilon_d)(\varepsilon_{xx}^r + i\varepsilon_{xx}^i + 2\varepsilon_d)}$$

Generalized Maxwell Garnett Equation for LSPR

Magneto-plasmonic resonance  
does not coincide with the SPR



## MO effects in Plasmonics materials?



### Kerr effect in dots

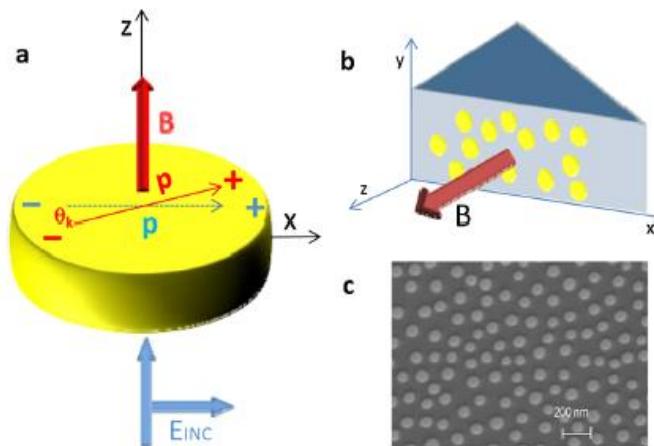


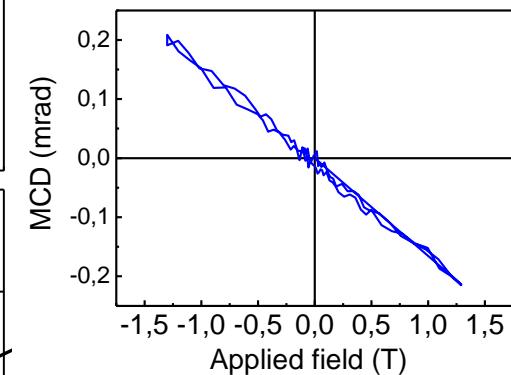
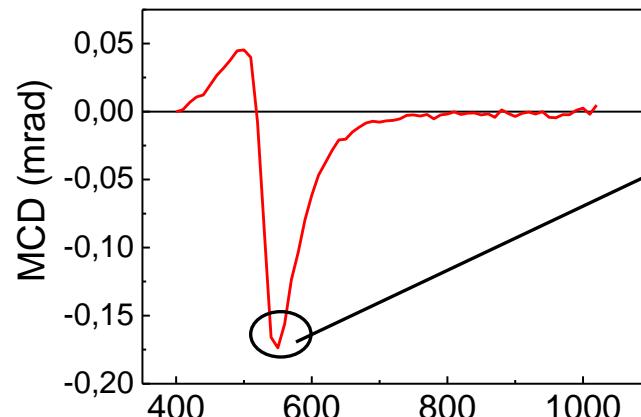
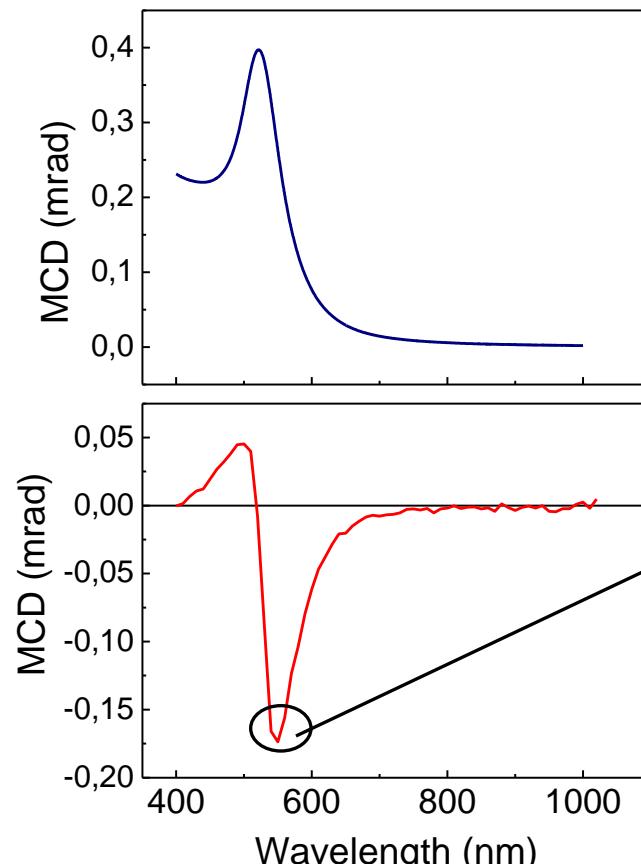
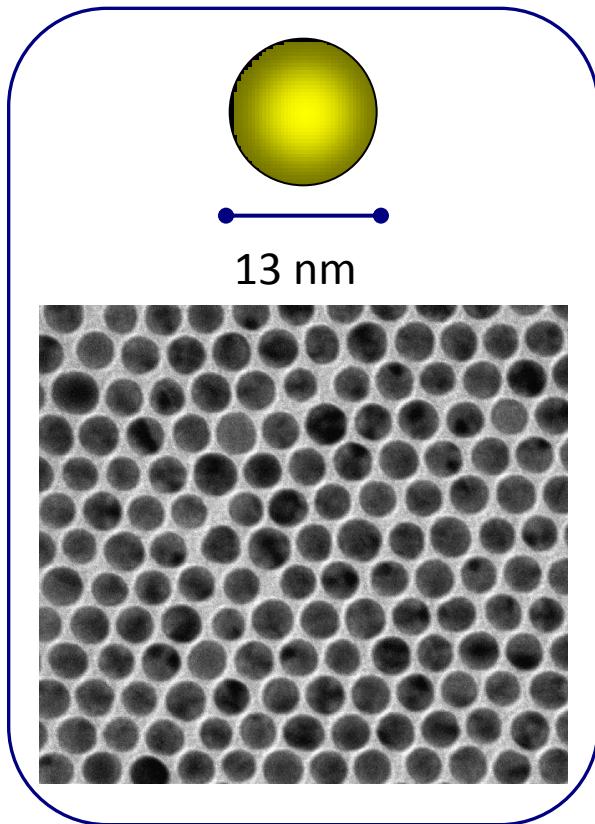
FIG. 1 (color online). (a) Schematic of the MO effect induced by the Lorentz force in a metal nanoparticle. (b) Magneto-optic Kerr polar experimental configuration. (c) SEM images of the gold nanodisk arrays.

Dephasing of the Electric field component

Modulation of SPR by the magnetic field

## MO effects in Plasmonics materials?

### MCD in NPs



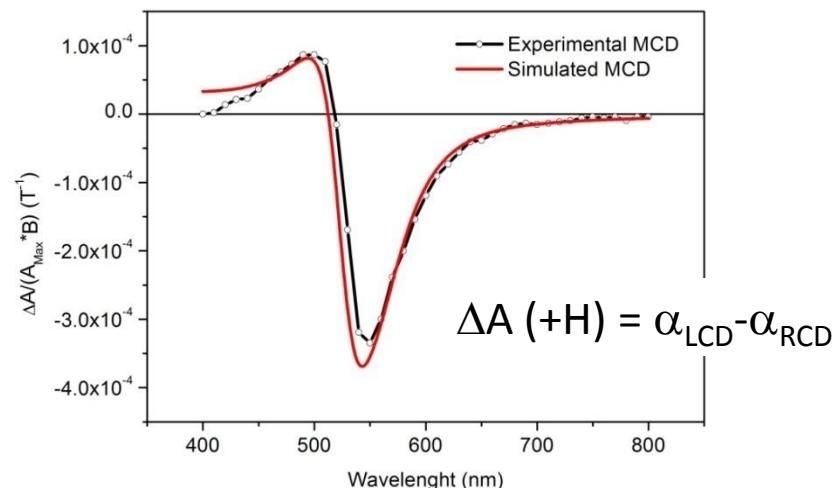
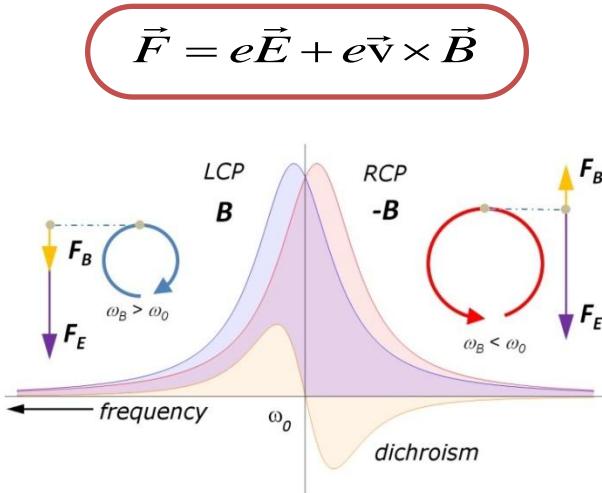
Modulation of SPR by the magnetic field



Amplification of the MO response

## LSPR with circular polarized light (Magnetic dichroism)

Circular polarized plasmons



Generalized Maxwell-Garnett for circular plasmons

Weick, Phys. Rev. B 83, 125405 (2011)

$$\alpha_B(\omega) = -\frac{\pi D^3}{2} \frac{(\epsilon(\omega) - \epsilon_m) + (f(\omega) - f_m)B}{(\epsilon(\omega) + 2\epsilon_m) + (f(\omega) - f_m)B}$$

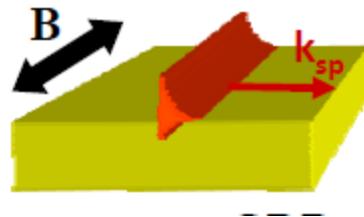
$$\omega_B = \omega_0 - \frac{B \Delta f_1(\omega_0)}{\left. \frac{\partial \epsilon_1}{\partial \omega} \right|_{\omega_0}} = \omega_0 - g(\omega_0)B$$

Modulation of SPR by the magnetic field

Amplification of the MO response

## MO effects in Plasmonics materials?

Also in SPP



■ TM polarization

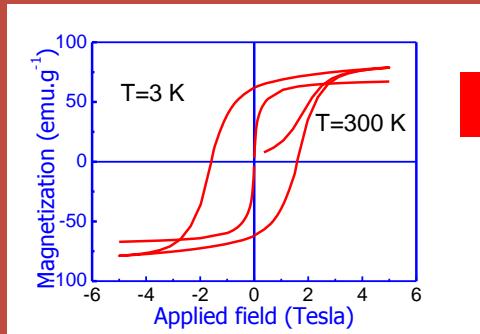
$$k_{sp} \approx \frac{\omega}{c} \sqrt{\frac{\epsilon}{\epsilon + 1}} \left( 1 - \frac{i\epsilon_{mo}}{(1 + \epsilon^2) \sqrt{-\epsilon}} \right)$$

$$k_{sp}(B) = k_{sp}^0 + \Delta k_{sp}(B)$$

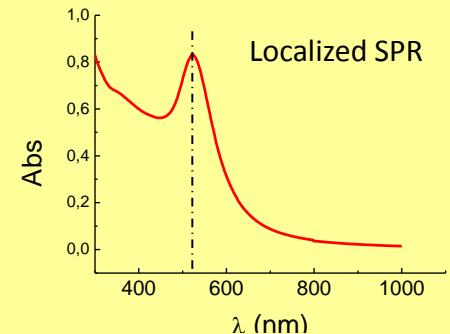
Au/air  $\Delta k/k \times B = 10^{-6}$   
Co/air  $\Delta k/k \times M = 10^{-4}$

MO effect is larger in Magnetic materials

## MAGNETIC + PLASMONICS



Metallic Magnetic NPs



Noble Metals

SPR in UV  
Damped

Very weak MO  
response

NO Spin polarization

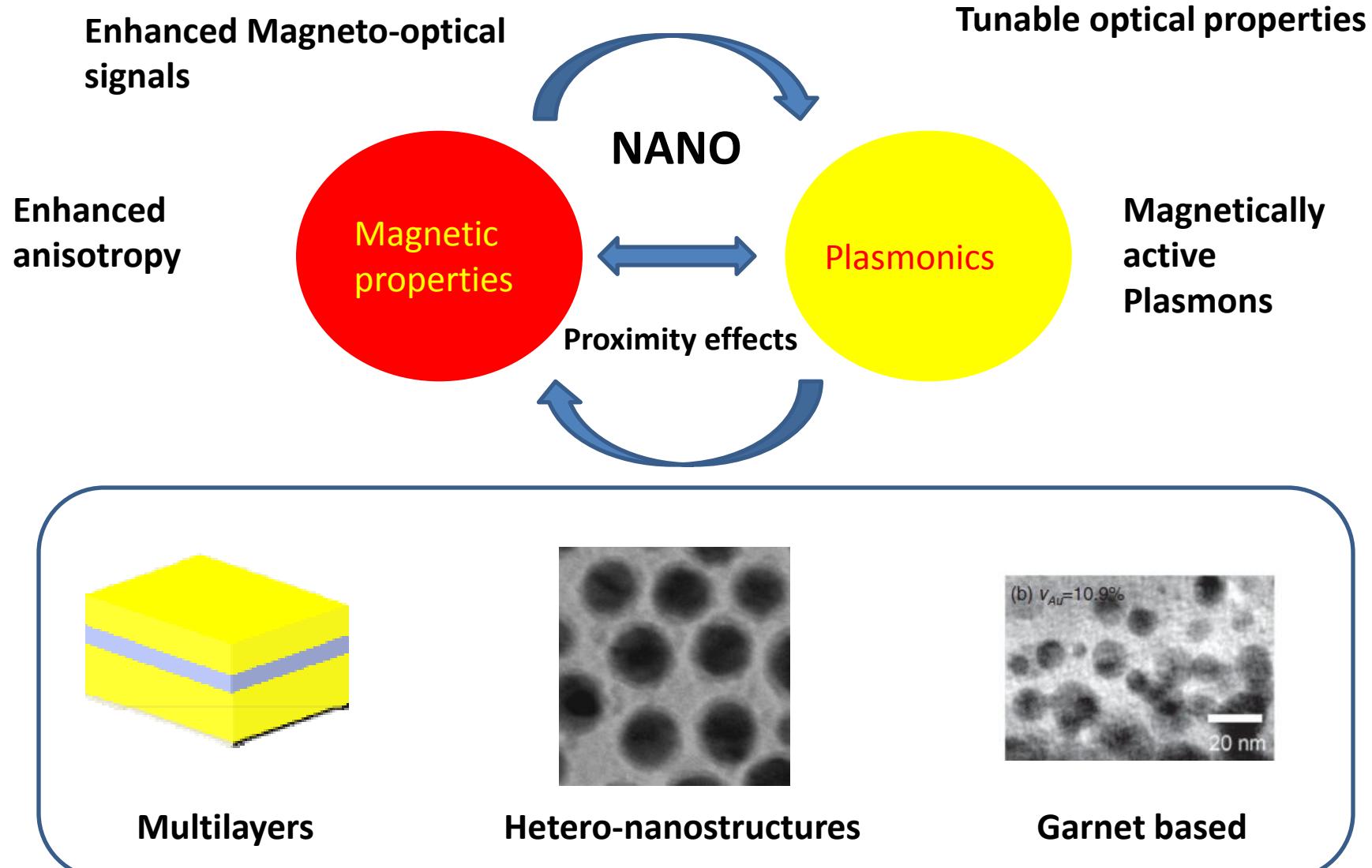
d-f localized bands

Both are not soluble

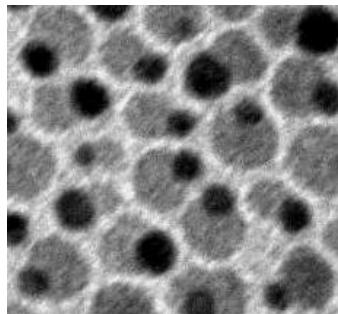
s bands (free electrons)

Hybrids Nanostructures

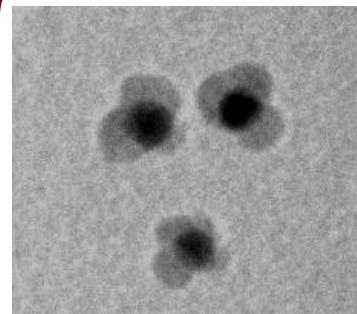
# Hybrid Magnetoplasmonics materials



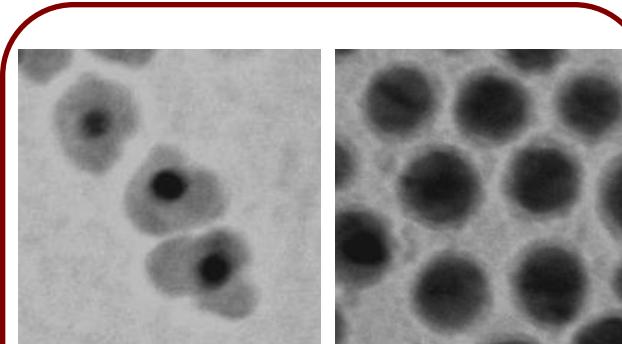
## Hetero-nanostructures



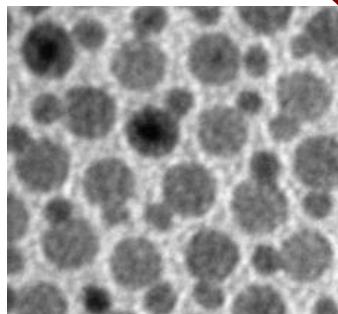
Gold-Iron oxide  
Heterodimers



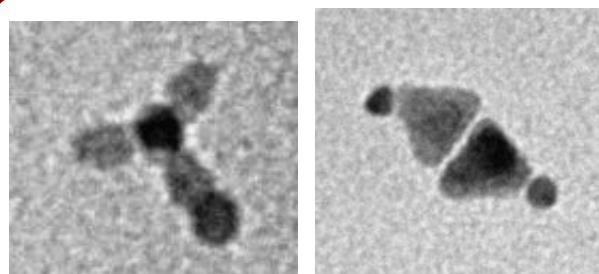
Gold-Iron oxide  
Flowers



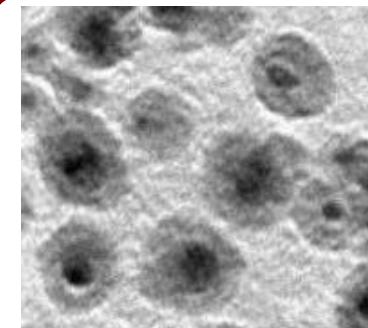
Gold@Iron oxide  
Core@shells



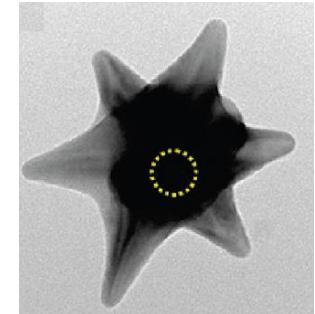
Silver-Iron oxide  
Heterodimers



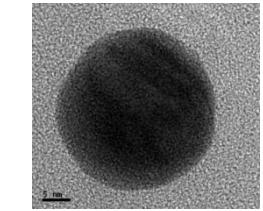
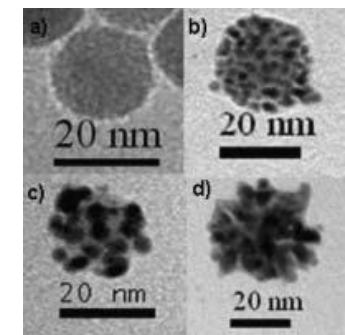
Iron oxide tetrapods & prisms  
With a silver sphere



Gold@cobalt ferrite  
Core@hollow shells

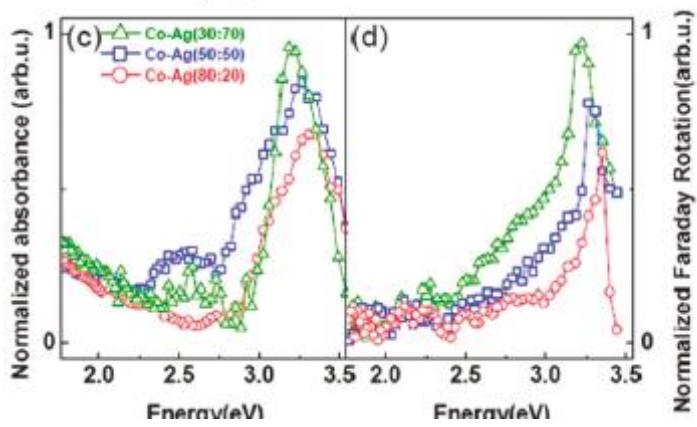
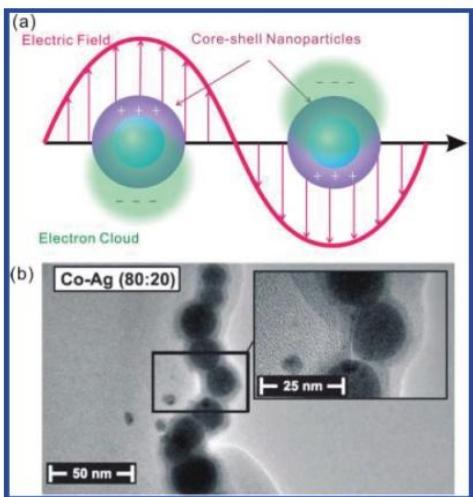


Iron oxide@gold  
Core@shells



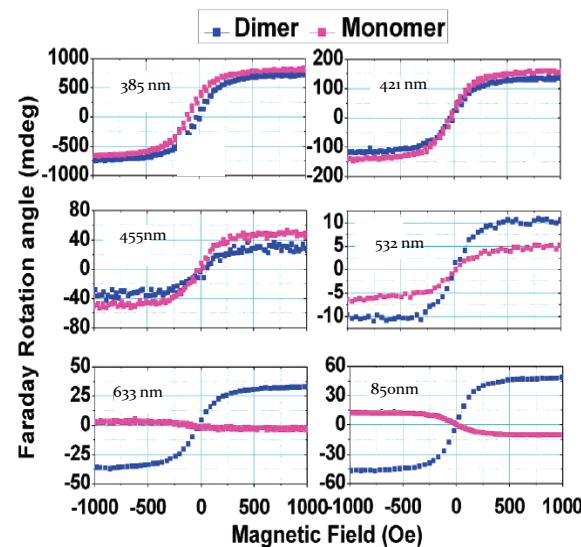
Gold-Iron Alloy

## Co@Ag NPs



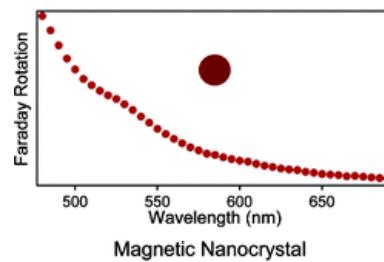
Wang Nano Letters 11 (2011) 1237

## Au @ Fe oxide



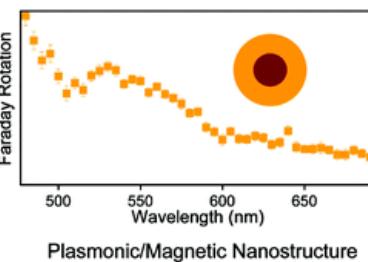
Li Nano Letters 5 (2005) 1689

## suPREMO



Magnetic Nanocrystal

## Au core @ ferrite shell

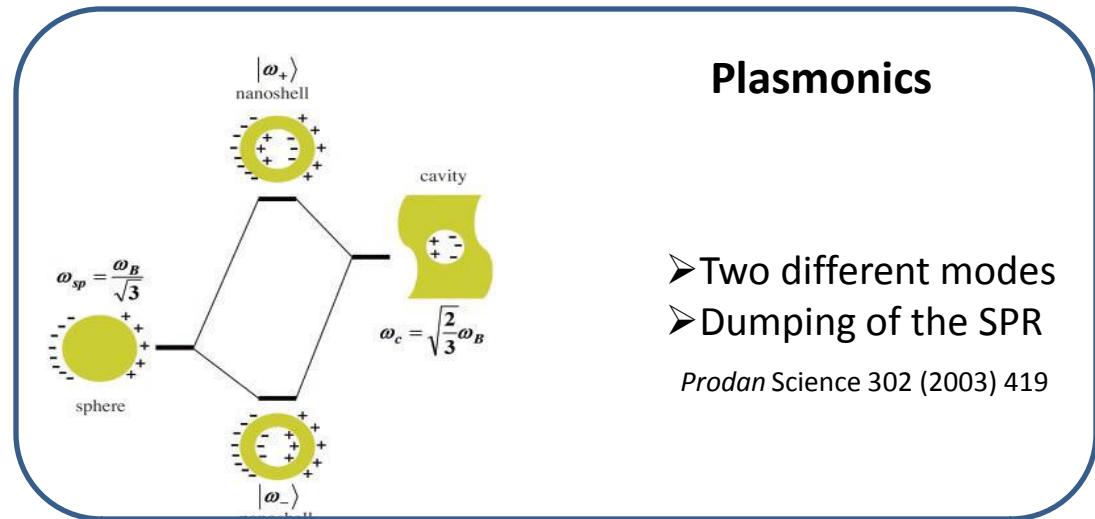
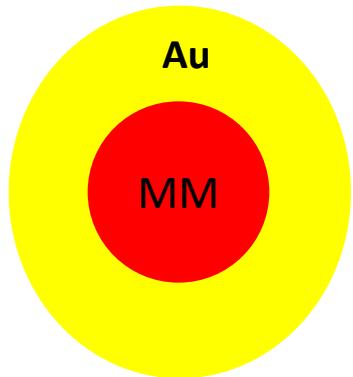


Plasmonic/Magnetic Nanostructure

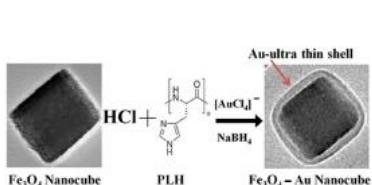
$\text{---} \gamma\text{-Fe}_2\text{O}_3$     $\text{---} \text{Au}$

Jain Nanoletters 9 (2009) 1644

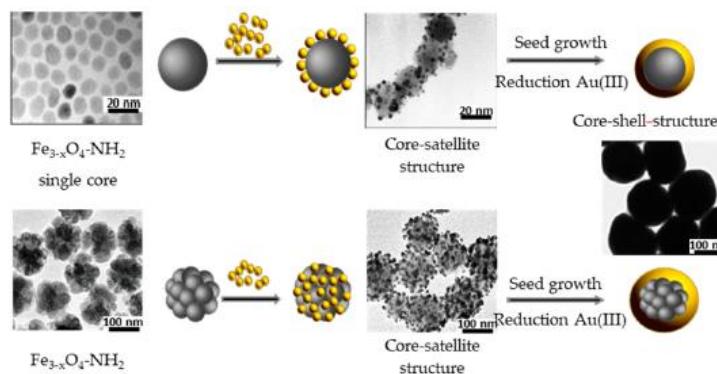
## Hetero-nanostructures: is it a good idea?



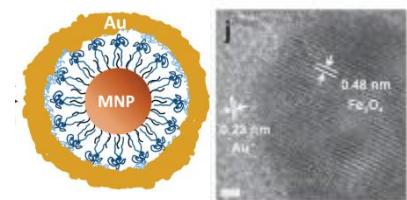
### Synthesis?



Mainly with oxides  
Metals?



Nguyen et al. Nanomaterials 8 (2018) 149



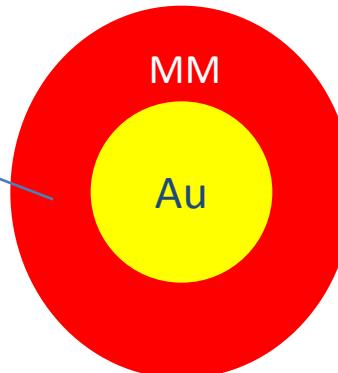
Jin, Nature Comm. 1 (2010) 41

Multishell structures  
could be easier

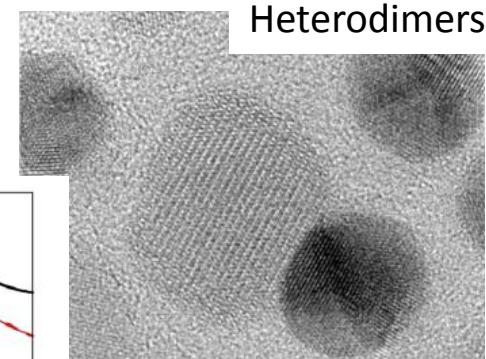
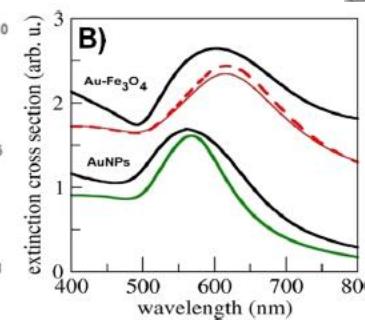
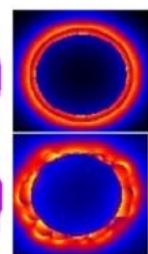
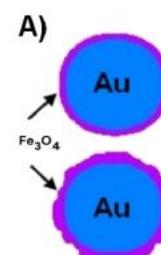
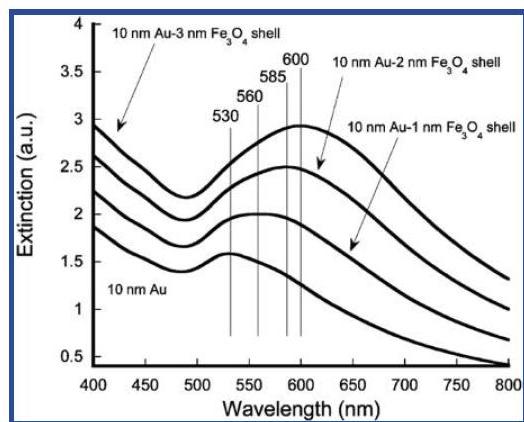
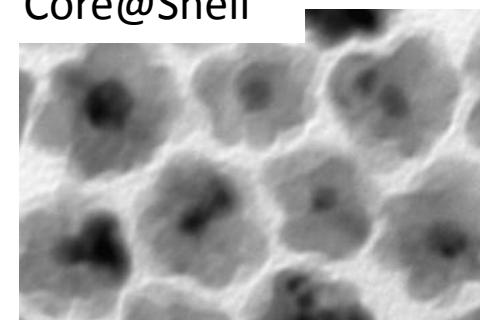
# Hetero-nanostructures, is it a good idea?

$$\alpha(\omega) = 4\pi\epsilon_d a^3 \frac{\epsilon_m(\omega) + \epsilon_d}{\epsilon_m(\omega) + 2\epsilon_d}$$

Most magnetic materials absorb in the VIS

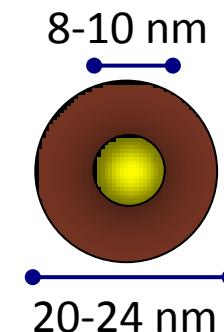
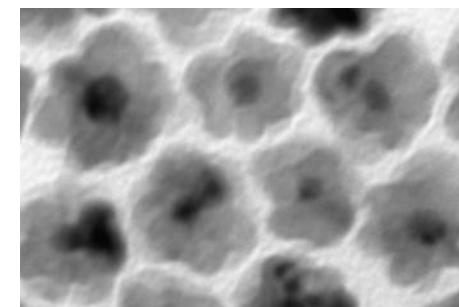
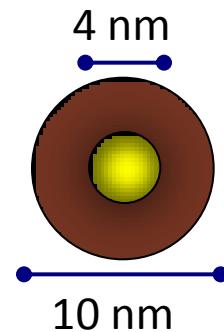
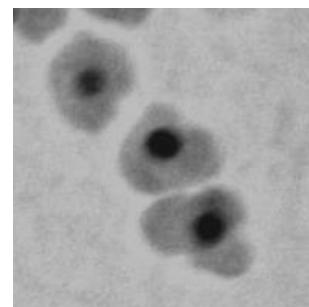
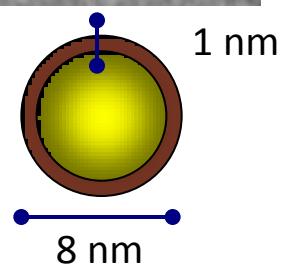
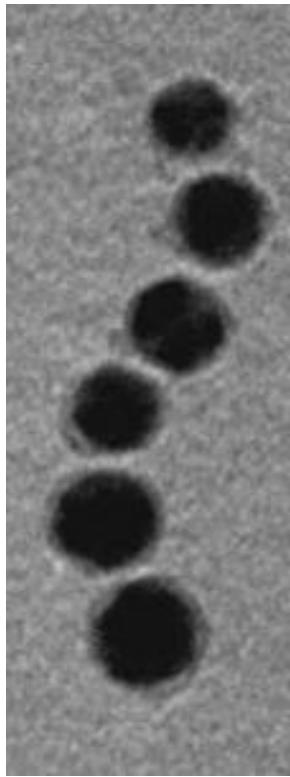


Core@Shell

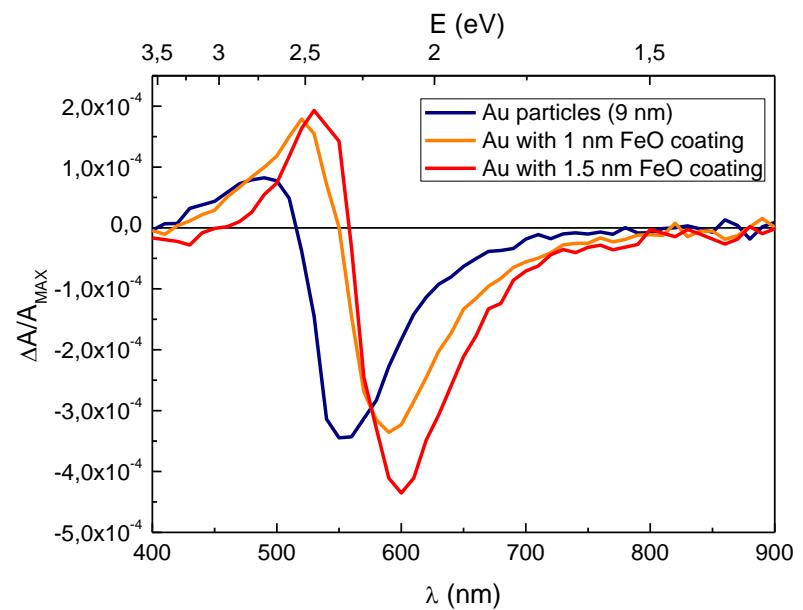
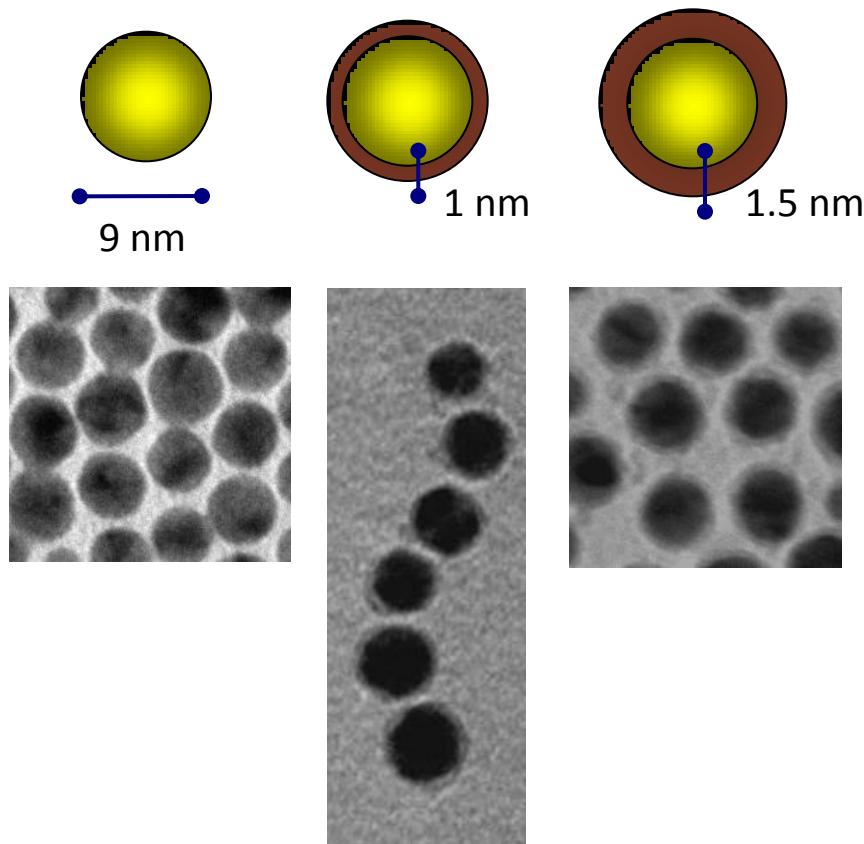


- ☞ Red Shift and damping of SPR!
- ☞ Problems in the reproducibility of the Nanostructures

## Au and Fe oxide Hetero-nanostructures

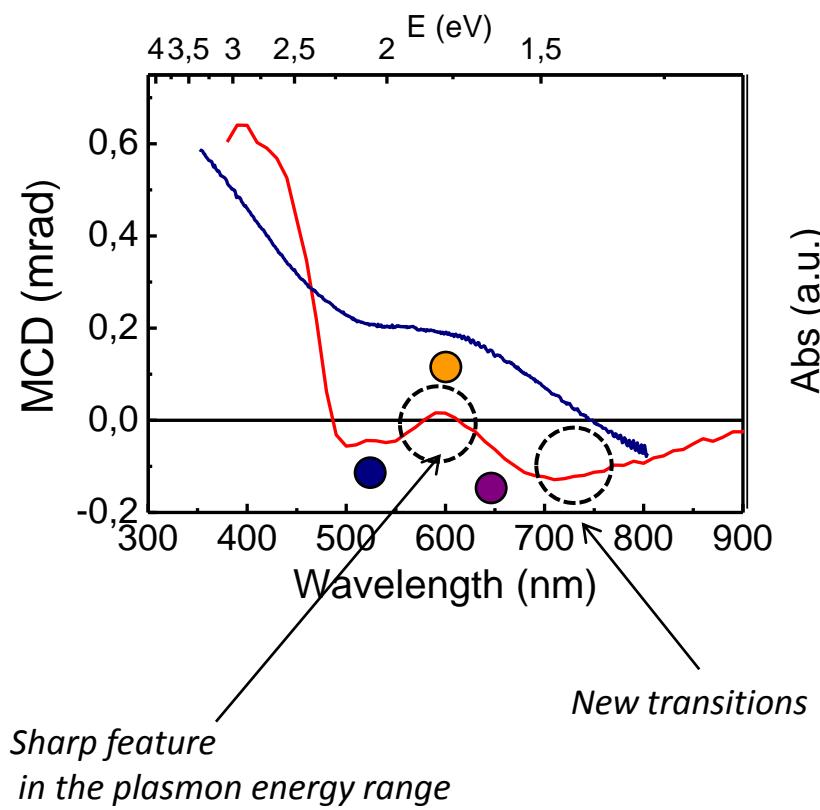
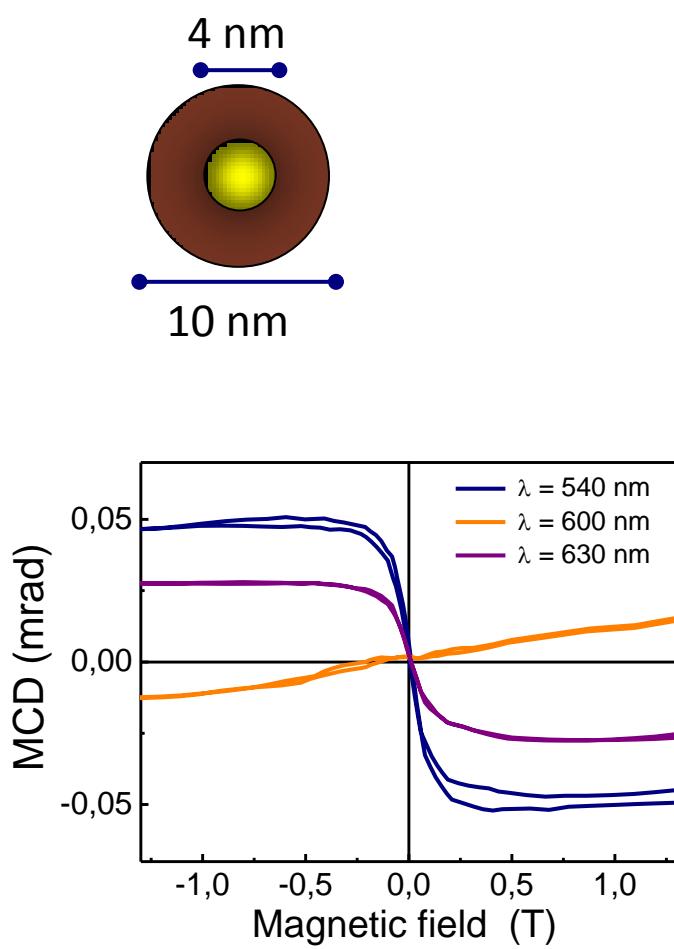


## Au and Fe oxide core@shell



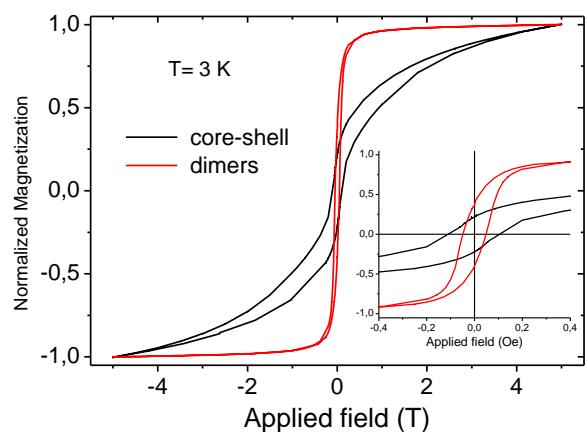
Pure plasmonics!!!

## Au and Fe oxide core@shell

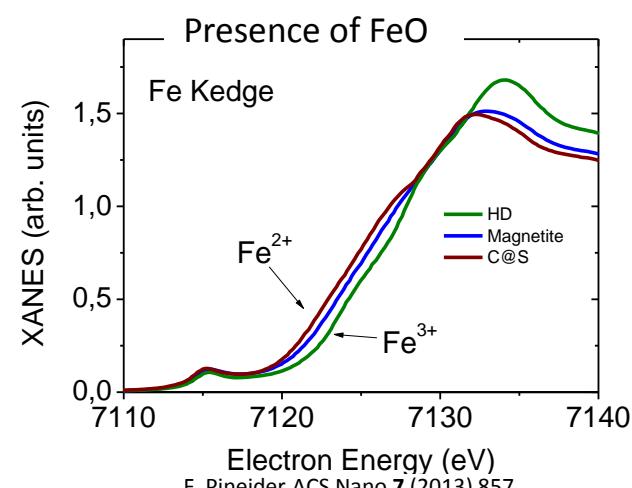


Superparamagnetic AND strong diamagnetic response!

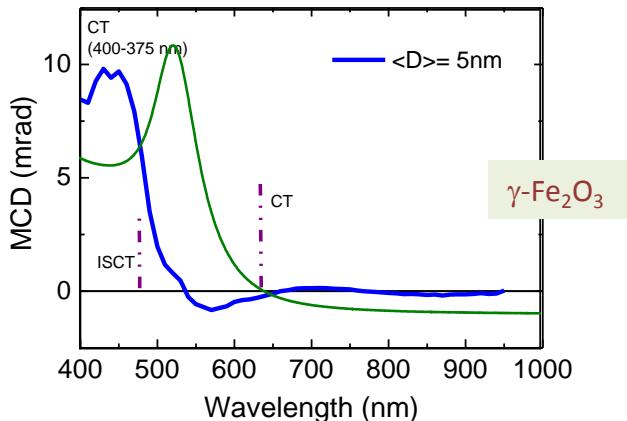
## Size and shape dependence



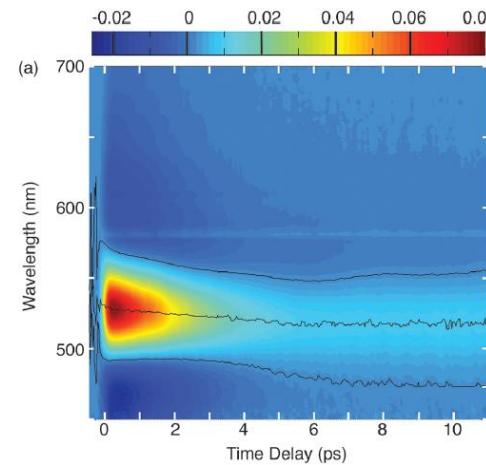
## Charge-transfer effects at interface



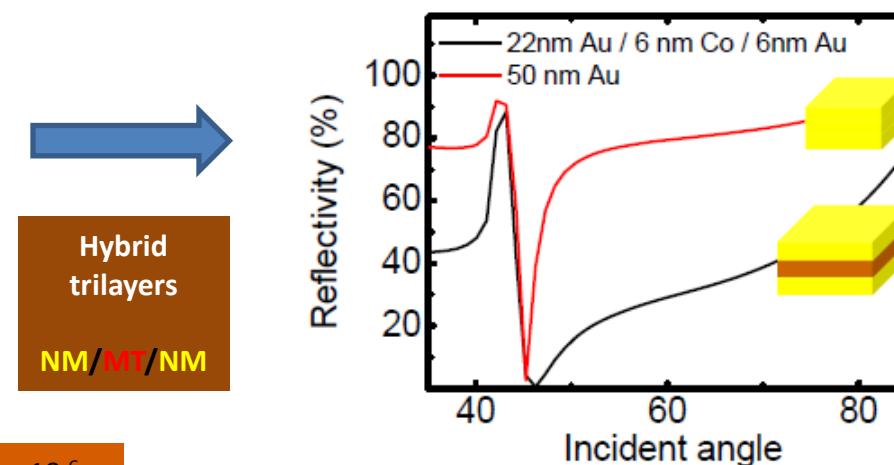
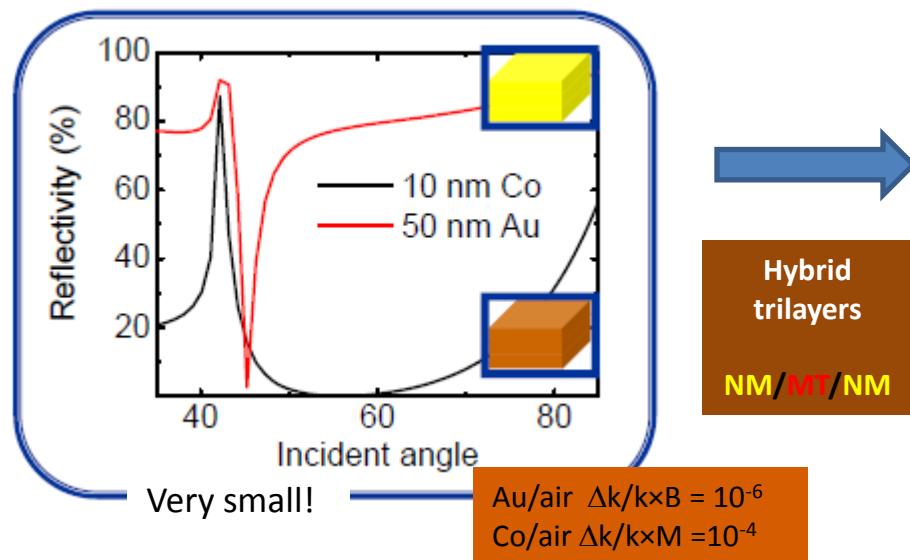
## Correspondence between MO transitions and SPR



## Electron diffusion or bleaching?

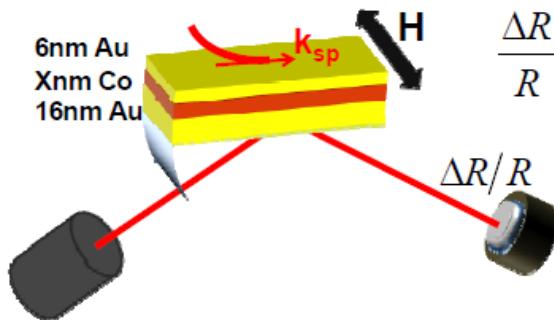


# Multilayers



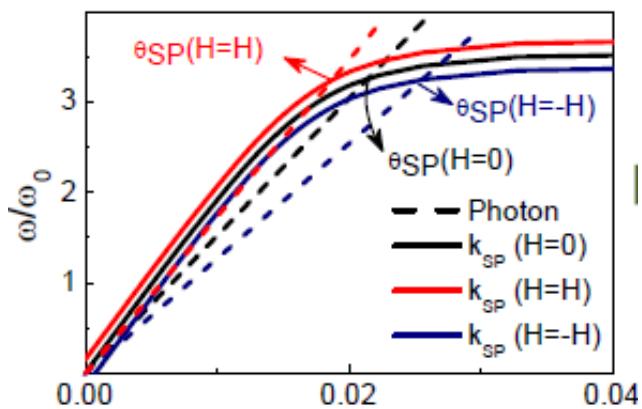
## Multilayers

The system:

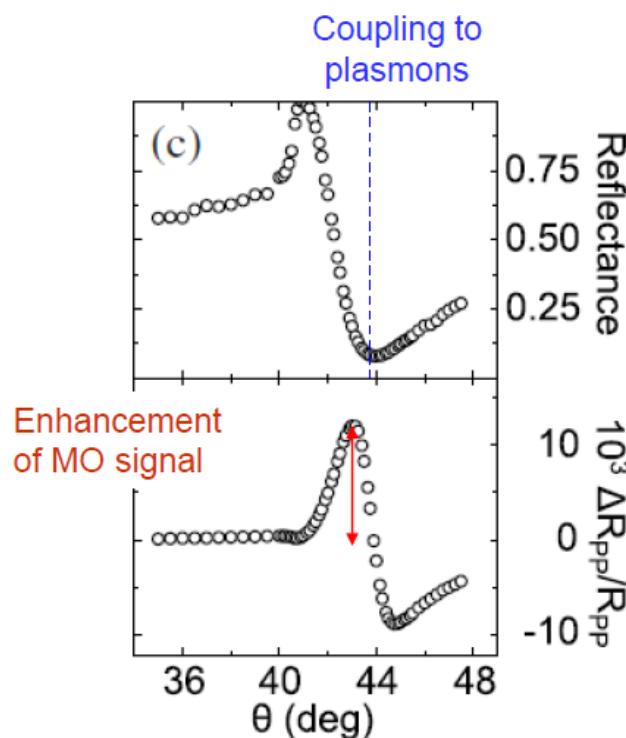


Transverse Kerr (TMOKE)

$$\frac{\Delta R}{R} = \frac{R(H) - R(-H)}{2R(0)}$$



$$k_{sp} = k_{sp}^0 \left( 1 + \frac{\Delta k_{sp}}{k_{sp}^0} B \right)$$

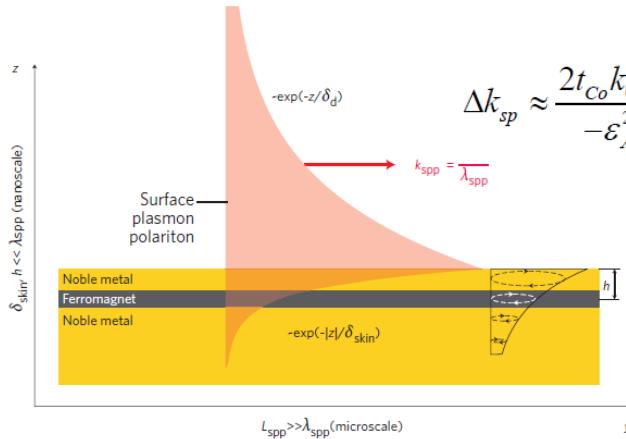


Large MOKE signal due to the field induced modulation of  $k_{sp}$

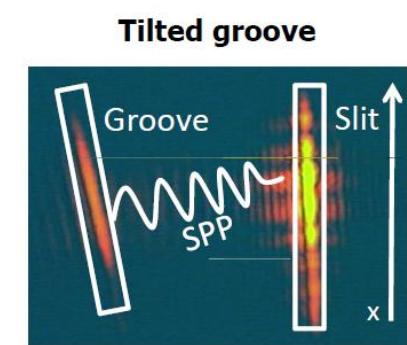
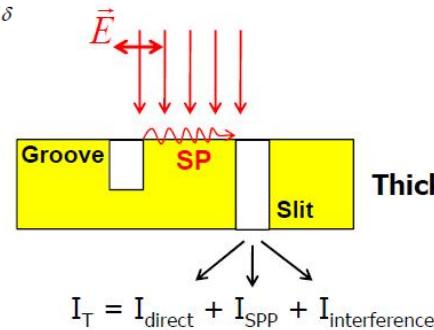
$$\frac{R_{pp}(M) - R_{pp}(-M)}{R_{pp}(0)} \approx -\frac{\frac{\partial R_{pp}(0)}{\partial \theta_{inc}}}{R_{pp}(0)} \Delta \theta_{min}$$

## Multilayers

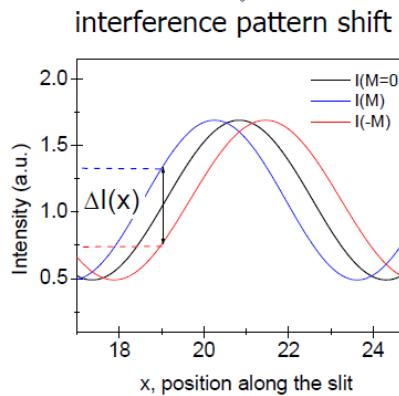
**Observation of Magnetic field SPP** (Telmnov Nat. Photonics 4 (2010) 107)



Telmnov Nat. Photonics 6 (2012) 728



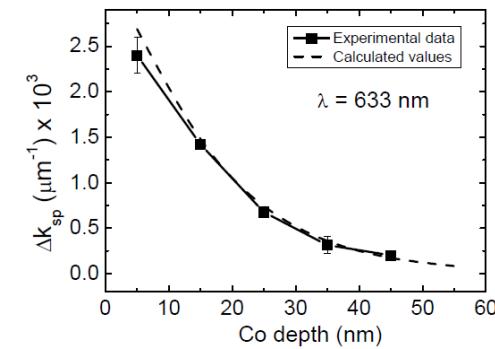
Magneto-plasmonic interferometer



Magnetic field control of Plasmonics

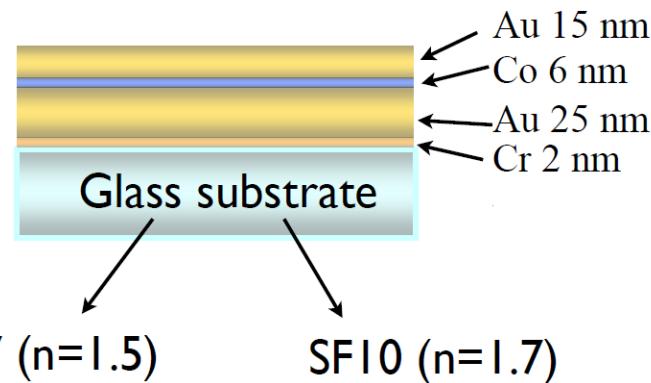


Active Optoelectronics devices



## Multilayers

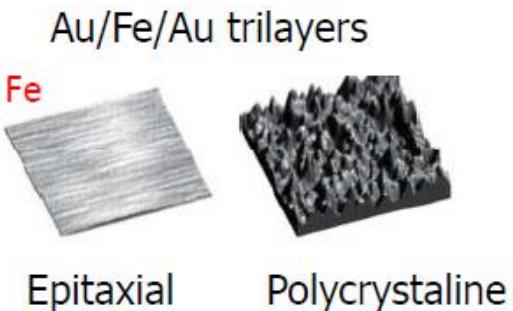
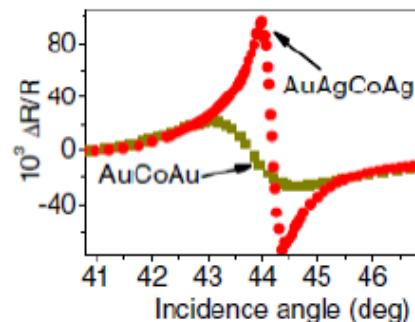
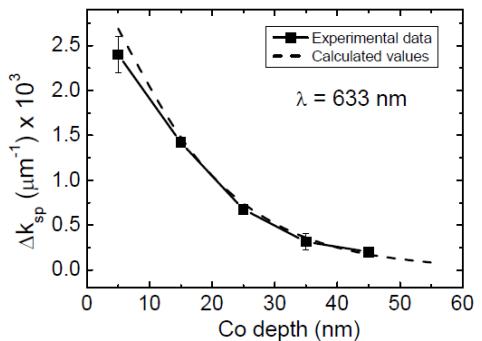
**Magnetic layer thickness**  
Increases MO contribution  
Increase Dumping



**Plasmonic materials**  
Better Ag than Au  
But oxidation

**Magnetic layer position**  
Better nearby surface  
But oxidation

**Quality of the films**  
Epitaxial growth  
Decreases roughness and interdiffusion  
Improve magnetic properties



## Applications

Multifunctional Nanomaterials

Biomedicine – Pharmacology- Catalysis

Nanomaterials with Enhanced MO Signals

Optoelectronics -Telecommunications

Magnetic field active plasmonics devices

Optoelectronics –Telecommunications

Spinplasmonics

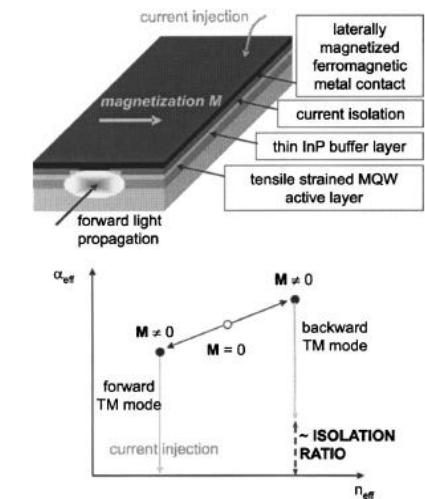
Plasmon assisted magnetic recording

Data Storage

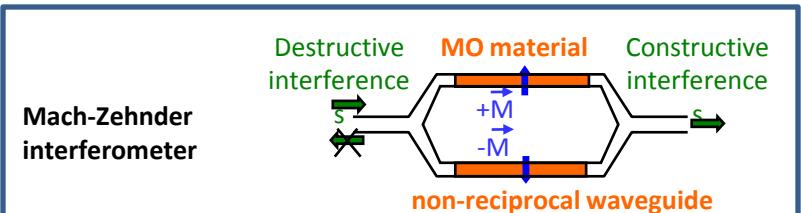
Sensors

Biomedicine – Pharmacology- Catalysis

Separation



Van Parys et al. APL 88 (2006) 071115

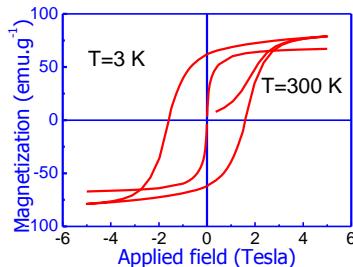


# Biomedical applications

Targeting -Delivery

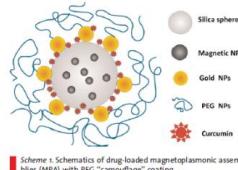
Diagnostics

Therapy



- Magnetic forces
- NMRi
- Hyperthermia
- Targeting
- Delivery
- Ultrasound imaging

## Multifunctional Magnetoplasmonic Nanoparticle Assemblies for Cancer Therapy and Diagnostics (Theranostics)<sup>a,b</sup>

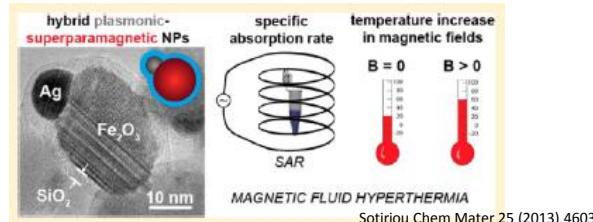


*Chen Macromol. Rapid Commun. 2010, 31, 228*

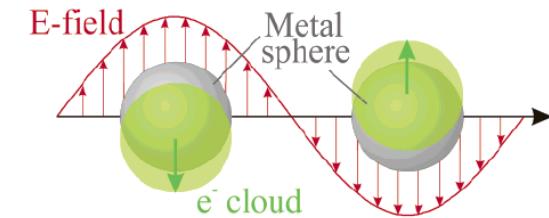
## Au-ultrathin functionalized core-shell ( $\text{Fe}_3\text{O}_4@\text{Au}$ ) monodispersed nanocubes for a combination of magnetic/plasmonic photothermal cancer cell killing<sup>†</sup>

Md. Abdulla-Al-Mamun,<sup>\*ab</sup> Yoshihumi Kusumoto,<sup>a\*</sup> Tohfatal Zannat,<sup>a</sup> Yuji Horie<sup>c</sup> and Hirotaka Manaka<sup>c</sup> RSC Adv. 3 (2013) 7816

## Thermal Energy Dissipation by $\text{SiO}_2$ -Coated Plasmonic-Superparamagnetic Nanoparticles in Alternating Magnetic Fields



Lim Nano Today 8 (2013), 98  
 Zhou J. Biomed. Nanotechnol. 10 (2014) 2921  
 Tran Anal Chem 2 (2018)  
 Nguyen Nanomaterials 8 (2018) 149



- Health & Bio & Pharma
- SERS
- VIS- photon Imaging
- Targeting
- Photothermal therapy
- Sensing
- Delivery

## Magnetic field manipulation



Clusters, beads, microspheres

### Magnetic Targeting –Delivery: DNA- Drug therapies

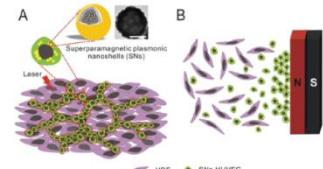
- Magnetophoretic
- Increase of local drug concentration
- Reduction of doses
- Larger retentivity

### Magnetic separation for diagnostics

### Magnetic seed for diagnostics

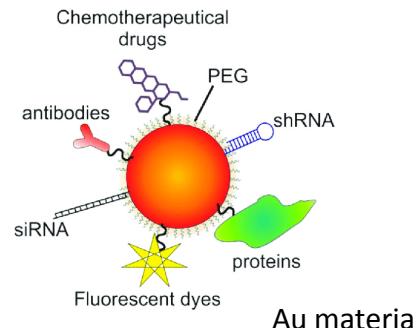
### Magnetic concentration

- Enhancement of optical signal

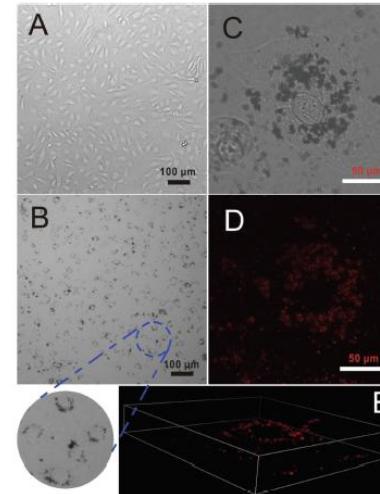


**Fig. 1** Schematic of (A) the plasmonic superparamagnetic nanoshell (SN)-HUVEC/HDF co-culture system and (B) the subsequent separation of two types of cells under an external magnetic field. Upon excitation of a pulse laser, the vascularization of HUVECs is visualized via two-photon luminescence imaging of SNs. The inset in panel (A) is a TEM image of a SN, and the scale bar is 100 nm.

## Inertness Functionalization

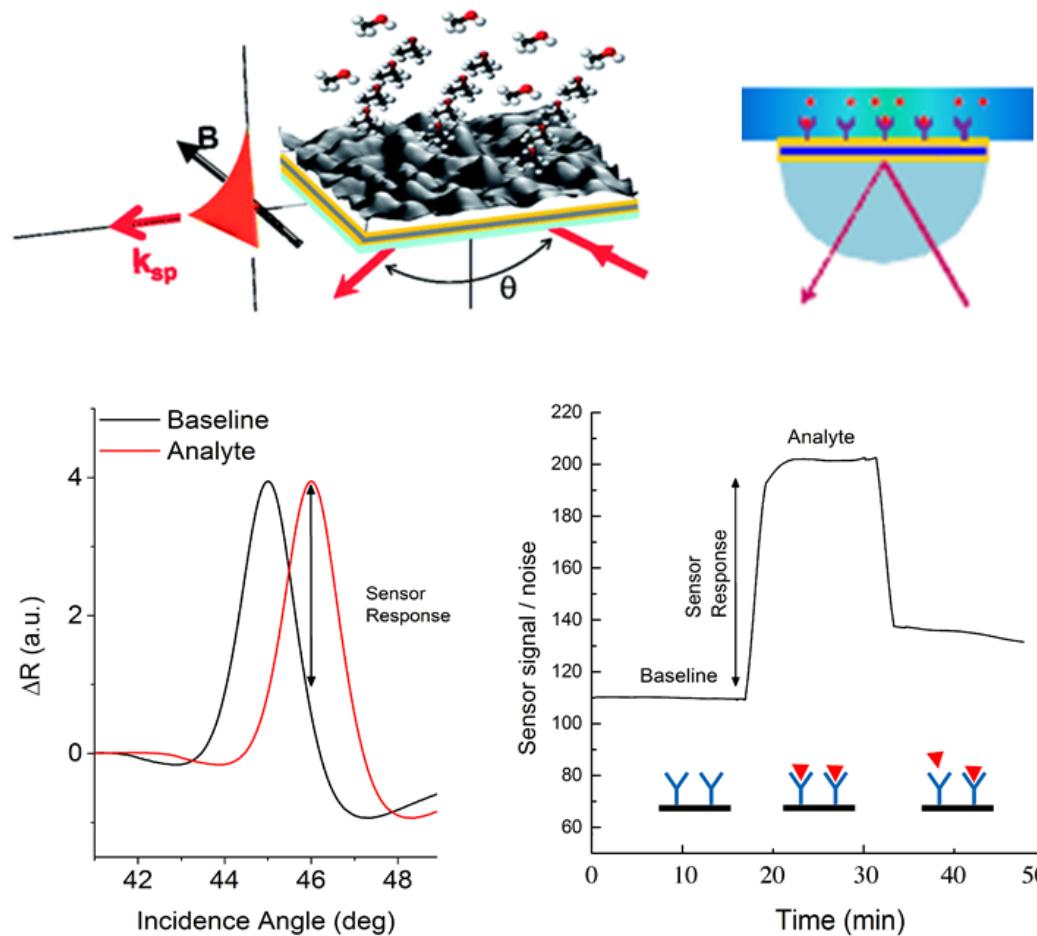


Overcome toxicity of Magnetic NPs  
Employment of efficient Magnetic materials



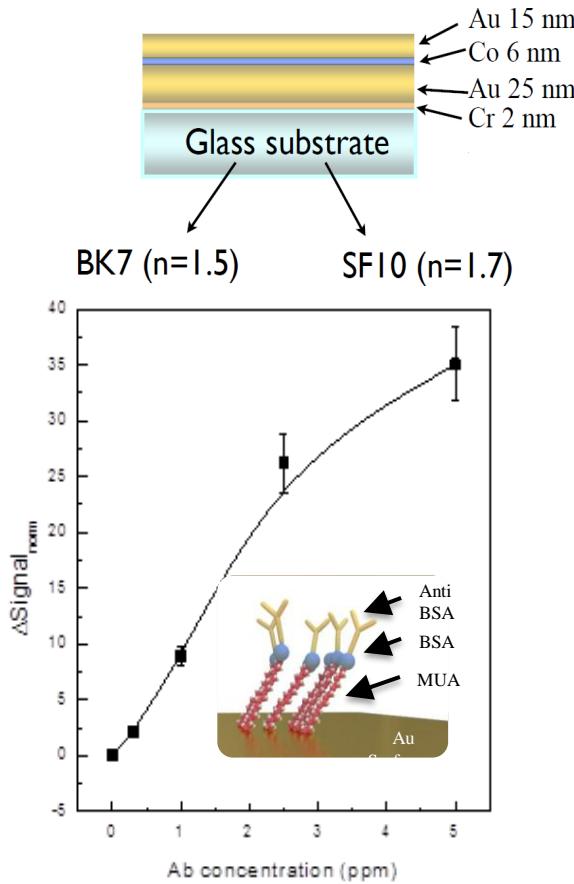
es of HUVECs cultured (A) without and (B) with  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Au}$  nanoparticles. The region in

## Diagnostics by ATR-SPR



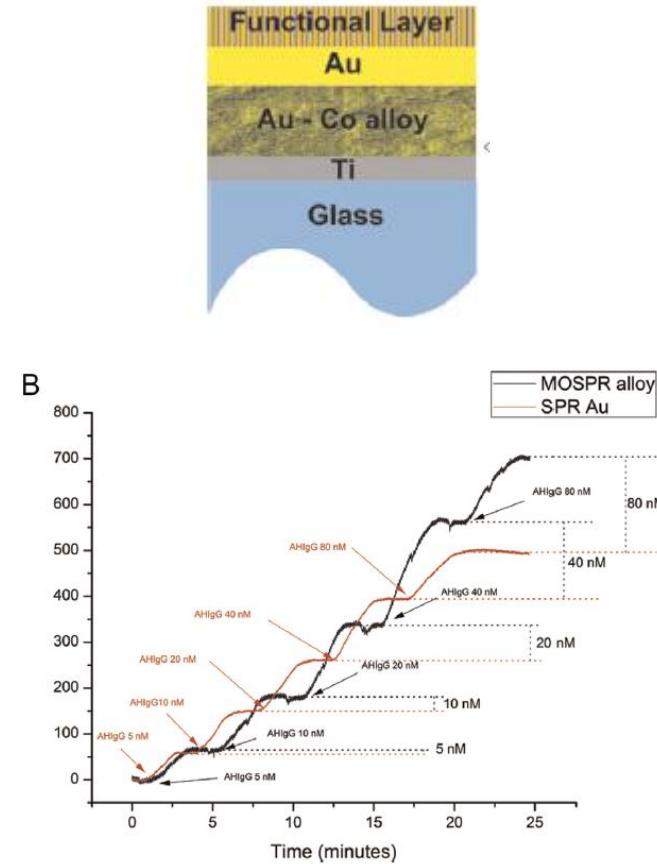
**Magnetic field assisted ATR devices  
have higher sensibility than conventional ones!**

## Diagnostics by ATR-SPR



Test with BSA and anti-BSA

Manera Sensors and Actuators B 179 (2013) 175



Test with HlgG and anti-HlgG

David Biosens Bioelec 63 (2015) 525

## Diagnostics by MO detection (LSPR)



### ARTICLE

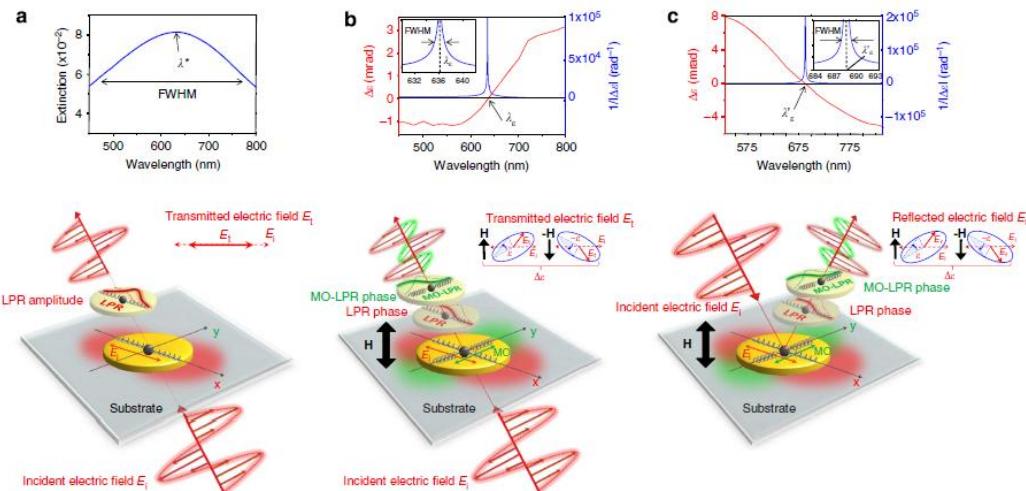
Received 13 Oct 2014 | Accepted 16 Dec 2014 | Published 2 Feb 2015

DOI: 10.1038/ncomm5750

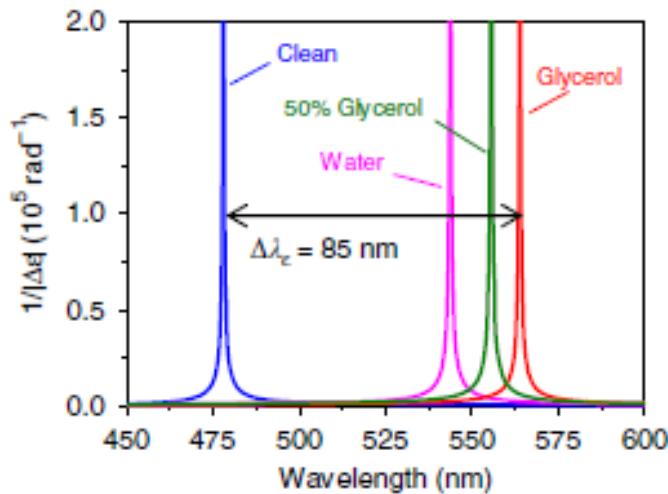
Ultrasensitive and label-free molecular-level detection enabled by light phase control in magnetoplasmonic nanoantennas

Nicolò Maccaferri<sup>1</sup>, Keith E. Gregorczyk<sup>1</sup>, Thales V.A.G. de Oliveira<sup>1</sup>, Mikko Kataja<sup>2</sup>, Sebastiaan van Dijken<sup>2</sup>, Zahleh Pirzadeh<sup>3</sup>, Alexandre Dmitriev<sup>3</sup>, Johan Akerman<sup>4,5</sup>, Mato Knez<sup>1,6</sup> & Paolo Vavassori<sup>1,6</sup>

Maccaferri Nat. Comm. 6 (2015) 6150

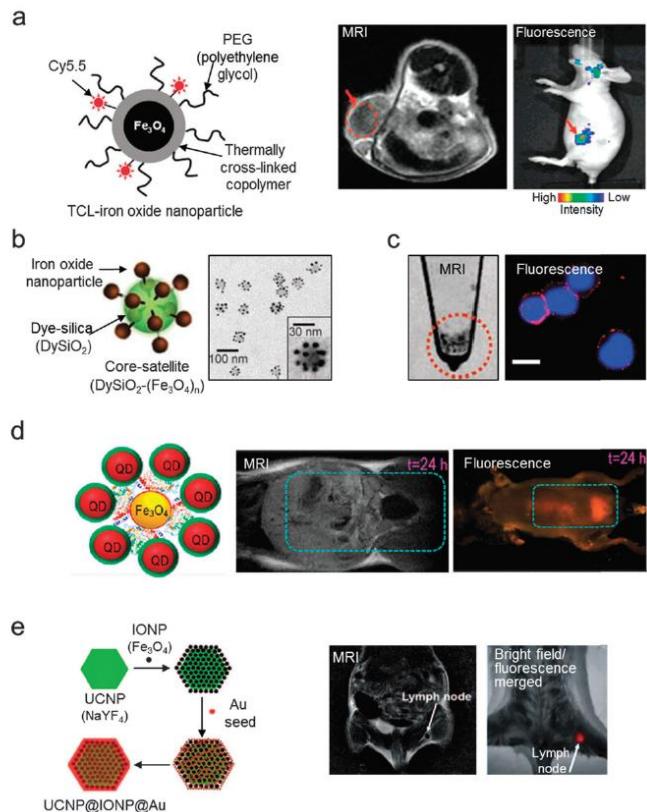


### Change of the $1/\Delta\epsilon$ with refraction index



Higher sensitivity and limit of detection values are reported in literature for plasmon-based sensors, which are achieved by application of fitting procedures<sup>30,31</sup>. We mention here that the application of fitting procedures of our data confirms the higher sensitivity of our approach as shown in the Supplementary Fig. 5. Indeed, a mass sensitivity in the sub-zg per nanoantenna, down to a few yg per nanoantenna, can be achieved through the application of fitting procedures opening a pathway to mass sensitivity corresponding to  $\sim 10$  molecules of PA-6.6 per disk (or, equivalently, of any material having  $n \sim 1.5$  and a density of  $\sim 1 \text{ g cm}^{-3}$ , which is the case of many polymers and biomolecules).

## Multimodal imaging



Shin Chem. Soc. Rev. 44 (2015) 4501

Different scales  
Background elimination  
Higher resolution

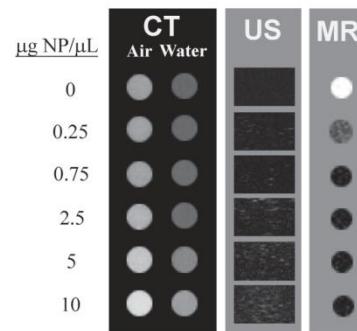
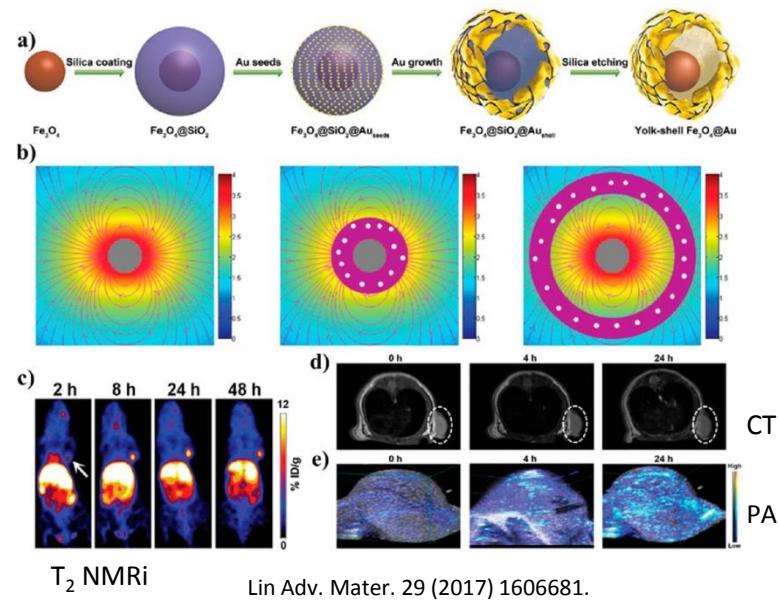
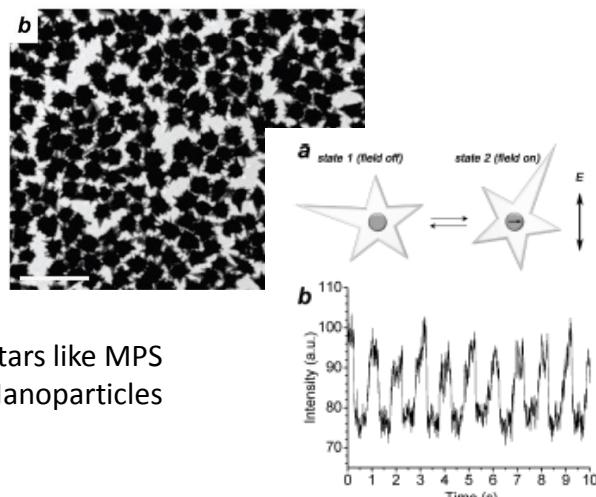


Figure 5. Comparison of the images obtained from each sample in X-ray CT (in air and in water), US (zoomed-in image from the focal plane of the images in Figure 3C) and  $\text{T}_2$ -weighted MRI.

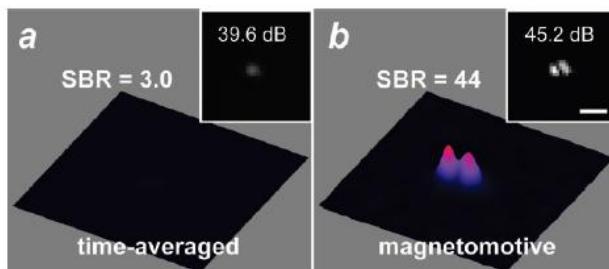
Carril Part. Part. Syst. Charact., 31, (2014) 81–87

## Magneto-motive imaging techniques

### Optical imaging

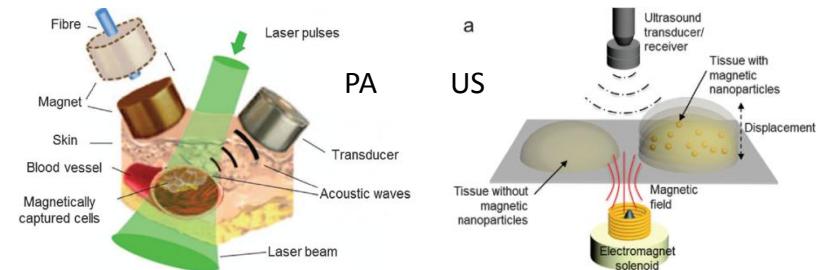


Rotating magnetic field gives rise to changes in the scattering



Song ACS Nano 4 (2010), 5163-5173

### Magneto-ultrasound photoacoustic detection



Shin Chem. Soc. Rev. 44 (2015) 4501

Li ACS Nano 9 (2015) 1964

Ovejero Microchimica Acta 185 (2018) 130

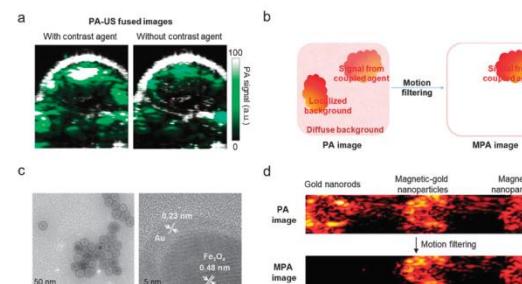


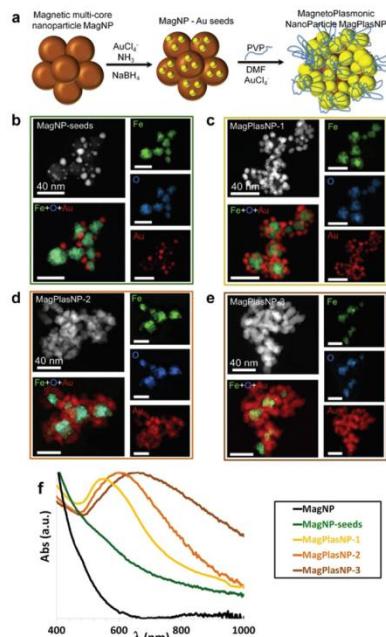
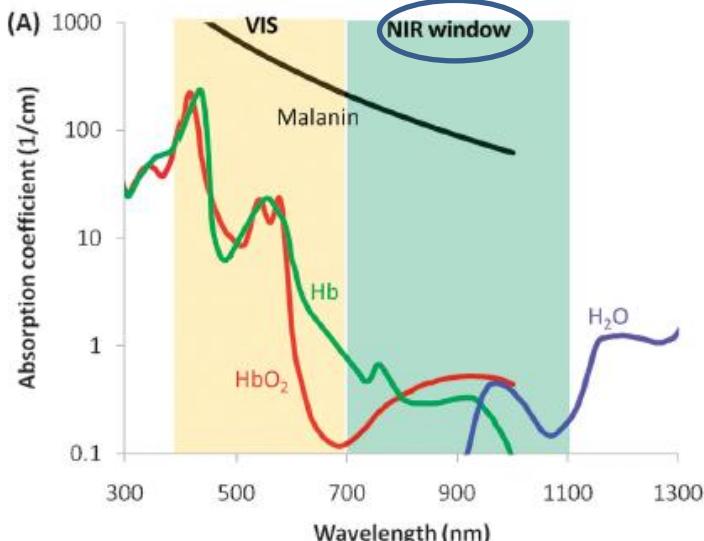
Fig. 10 Photoacoustic (PA) imaging accuracy enhancement via magneto-photoacoustic (MPA) imaging. (a) Conventional PA-US dual-modal imaging of tumors in a mouse with the PA contrast agent shows an increase of the PA signal (green). Non-negligible PA signals, which originate from background photoacoustic absorbers, are also observed in PA-US image without a contrast agent. (b) Schematic illustration of the background signal elimination via a motion filtering process. Only magnetic nanoparticle-based imaging agents that respond to a pulsed magnetic field can be distinguished from the background photoacoustic absorbers. (c) TEM images of the magnetic-gold nanoparticles. (d) Magnetic-gold nanoparticles and magnetic nanoparticles show strong MPA signals, while the signals from the gold nanorods that mimic the background are completely eliminated. (a) Reprinted with permission from ref. 49. Copyright 2010 American Chemical Society. (b-d) Reprinted with permission from Macmillan Publishers Ltd: ref. 7, copyright 2010.

Evertsson IEEE Trans ultrason Ferroelectr Freq Control. Control 61 (2014) 1276

# Magnetoplasmonics-Applications

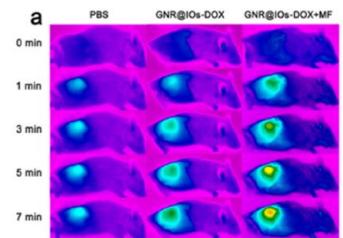
## Magnetoplasmonics for Imaging

VIS light penetration is limited to the skin



Espinosa Nanoscale 7 (2015) 18872

## For Photothermal therapy



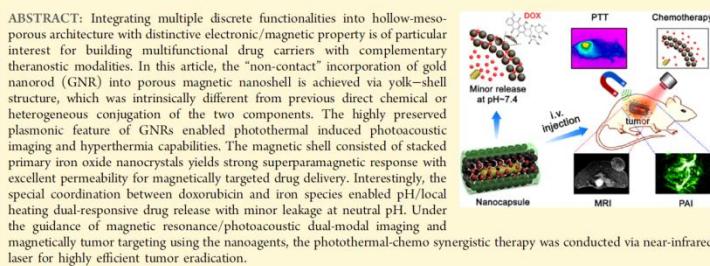
Huang Chem. Mater. 28 (2016) 5896

### Magneto-Plasmonic Nanocapsules for Multimodal-Imaging and Magnetically Guided Combination Cancer Therapy

Liang Huang<sup>†</sup>, Lijiao Ao<sup>†</sup>, Dehong Hu<sup>†</sup>, Wei Wang, Zonghai Sheng, and Wu Su<sup>\*</sup>

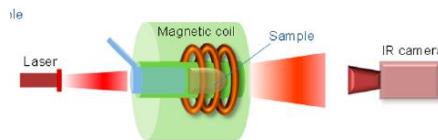
Guangdong Key Laboratory of Nanomedicine, Institute of Biomedicine and Biotechnology, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, P. R. China

Supporting Information



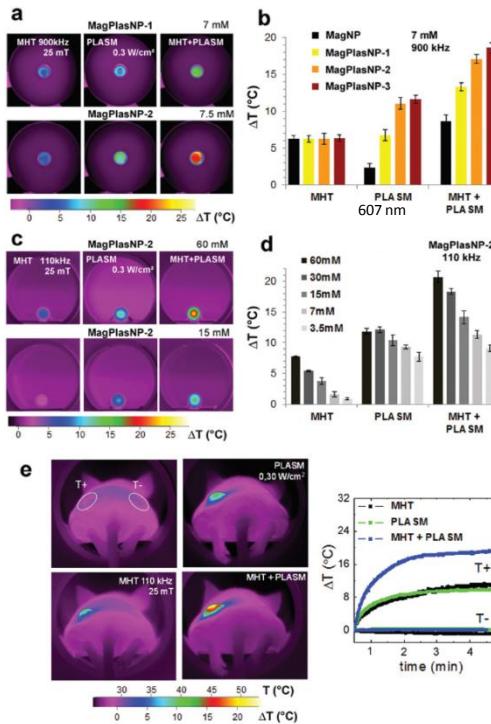
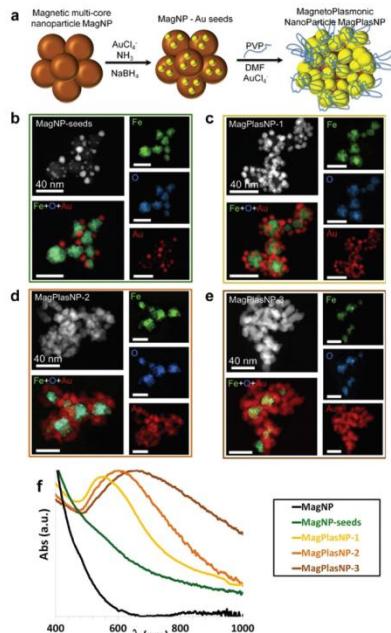
# Magnetoplasmonics-Applications

For Photothermal + Magnetic hyperthermia therapy



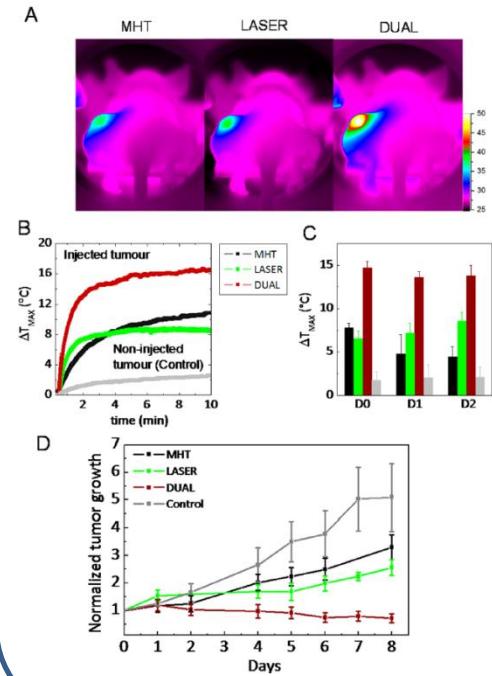
## MPs NPs

Espinosa Nanoscale 7 (2015) 18872



## Magnetic NPs

Espinosa ACS Nano 10 (2016) 2436

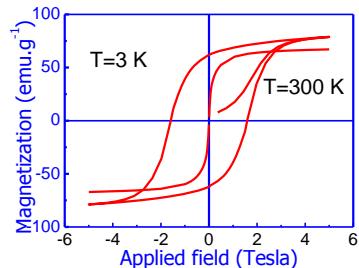


# Biomedical applications

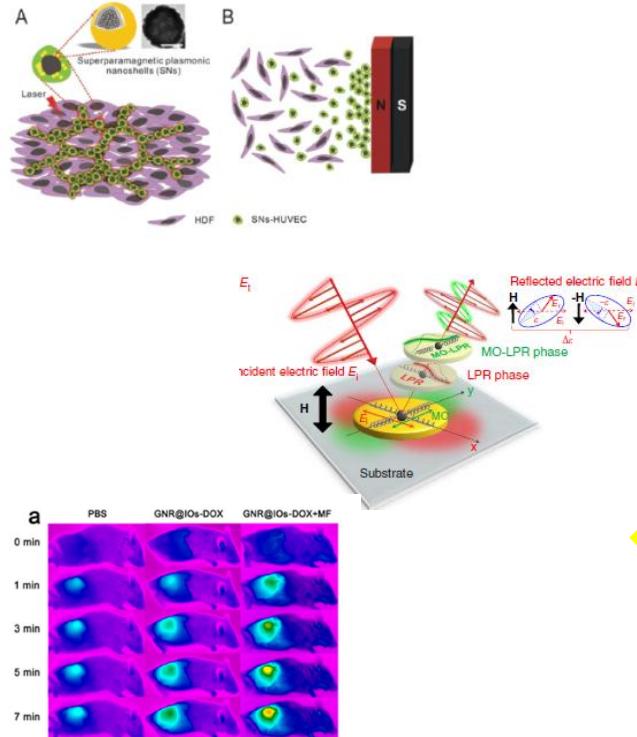
## Targeting

## Diagnostics

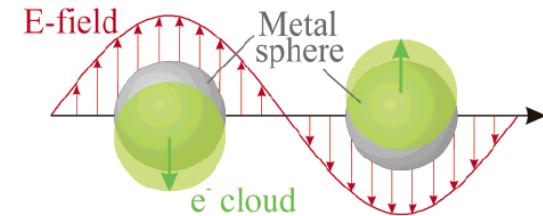
## Therapy



- Magnetic forces
- NMRI
- Hyperthermia
- Targeting
- Delivery
- Ultrasound imaging



- Improvements in targeting-diagnostics
- Multimodal diagnostics and imaging
- MO detection - MSPR
- Magneto-motive imaging
- Magnetic and thermal therapy



- Health & Bio & Pharma
- SERS
- VIS- photon Imaging
- Targeting
- Photothermal therapy
- Sensing
- Delivery

## The people

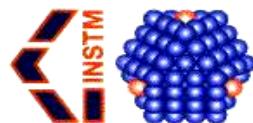
### IMEM

F. Vita  
F. Casoli  
S. Fabbrici  
F. Albertini  
P. P. Lupo (ex)



### INSTM – LAMM

G. Campo  
E. Fantechi  
C. Innocenti  
A. Caneschi  
F. Pineider (Univ. Pisa)  
V. Bonanni (Milano, ELETTRA)  
R. Novak (ex)  
L. Bogani (ex)



### CNR

C. Sangregorio (ICCOM)  
L. Cavigli (ICCOM)  
R. Rella (IMM)  
M. G. Manera (IMM)



Email: [cesar.dejulian@imem.cnr.it](mailto:cesar.dejulian@imem.cnr.it)

### Univ. Pavia

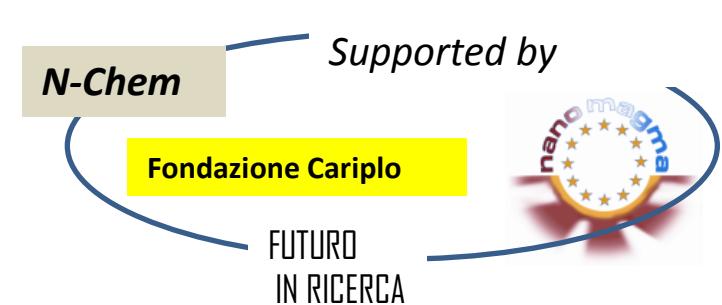
P. Ghigna

### Univ. Lecce

D. Cozzoli

### Univ. Milano

A. Lascialfari  
M. Scavini  
P. Masala



# **Thanks for your attention**