Chirality in low-cost plasmonics

DIPARTIMENTO DI SCIENZE
DI BASE E APPLICATE
PER L'INGEGNERIA

SAPIENZA
UNIVERSITÀ DI ROMA

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nonlinear photonics lab

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NanoInnovation 2020, 15 – 18 September 2020, Rome, Italy

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- Chiral effects in hybrid metal-polystyrene metasurfaces
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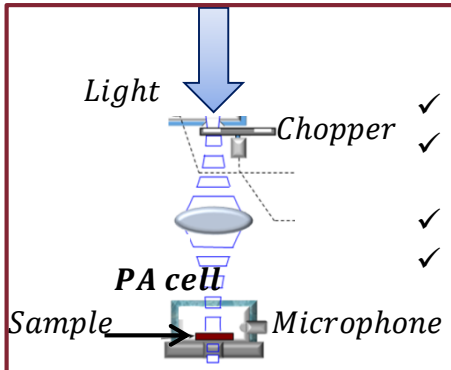
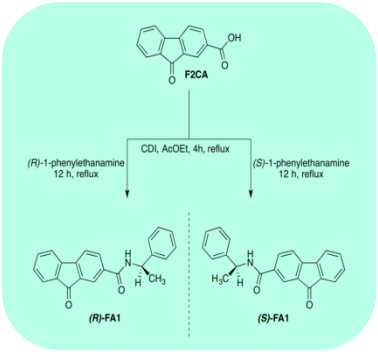


@SBAI

- ✓ Photo-acoustic technique
- ✓ Widely tunable near-IR laser **Chameleon Ultra II**
- ✓ Photo-deflection technique
- ✓ Design and optimization



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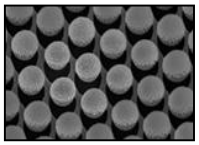
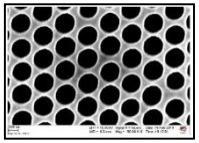
- ✓ Synthesis of chiral molecules





In collaboration with:

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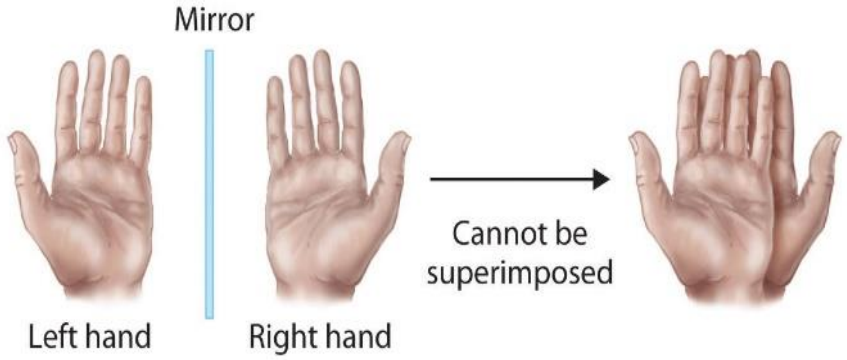
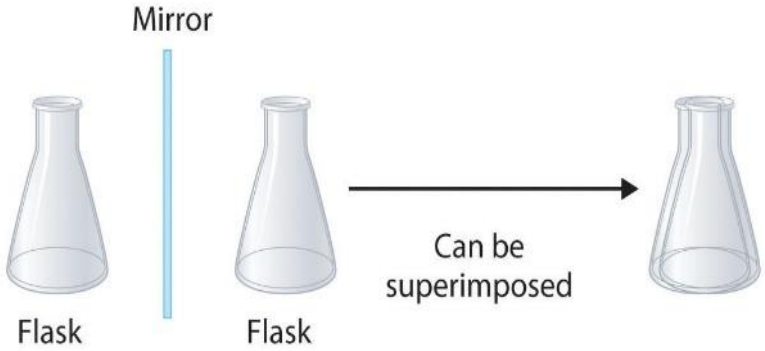
Motivation to study chirality

Chirality (or handedness) is the lack of mirror symmetry.

An object is chiral if it cannot be superimposed on its mirror images



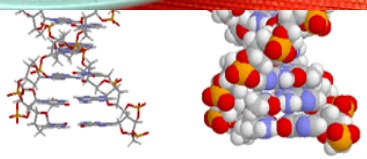
(a) Chiral objects



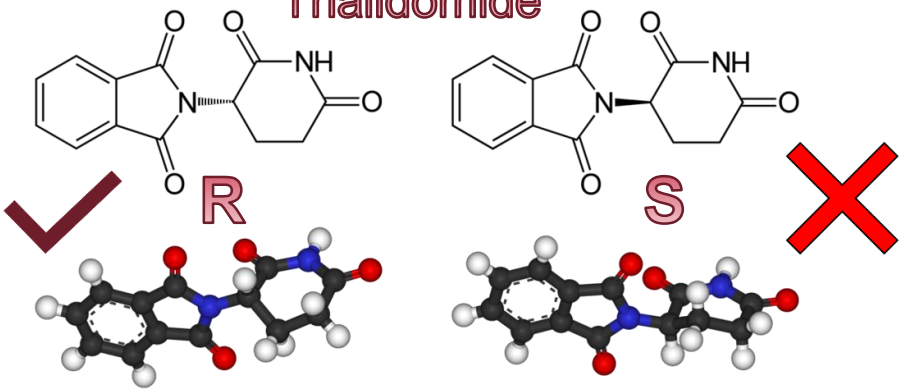
(b) Achiral objects

Chiral world:
- -DNA
- -Sugars
- -Amino-acids
- -Enzymes
- -Drugs

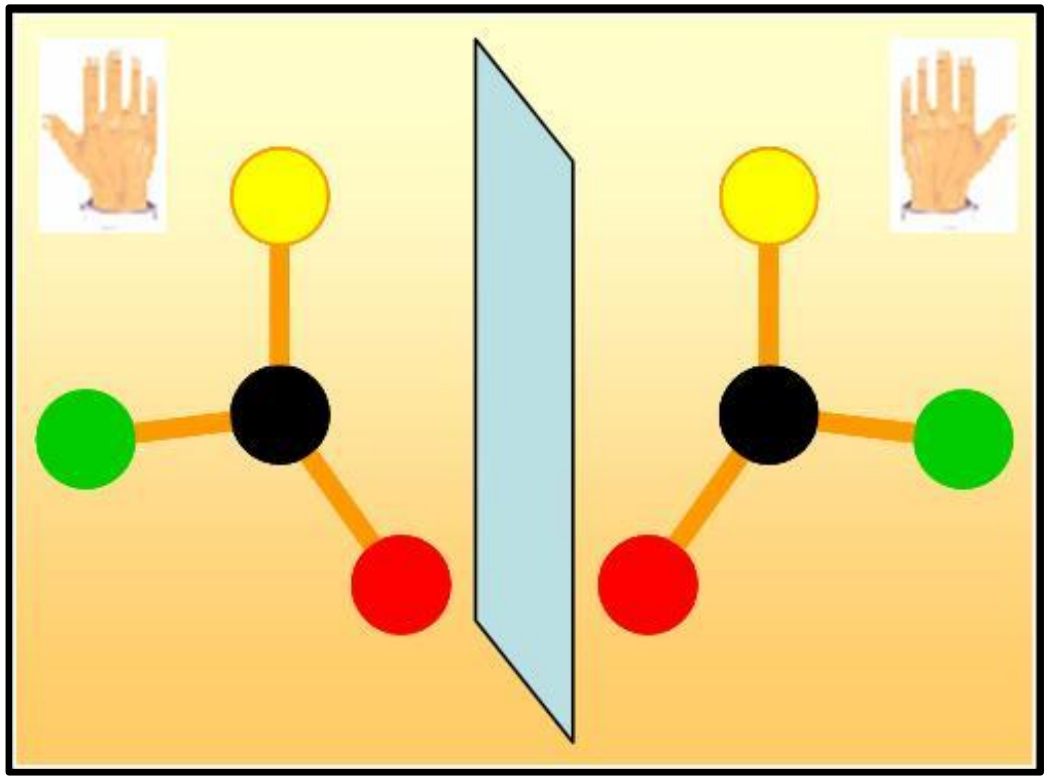
Enantiomers



Thalidomide



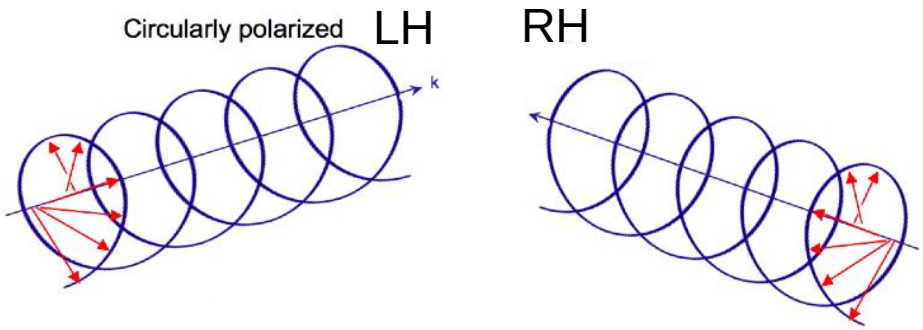
The simplest chiral system: a triad of nonplanar vectors



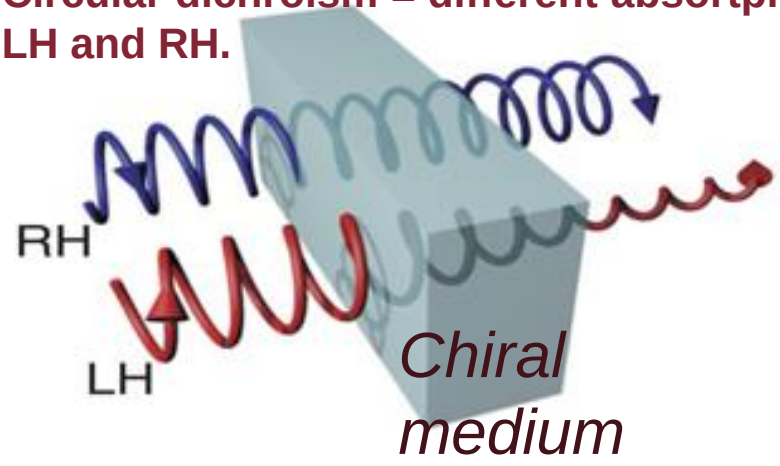
No rotational or translational transformation can reproduce the original triad!

Motivation to study chirality

In Optics, circular polarization is also chiral – left or right-handed!



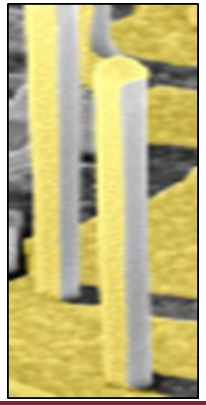
Circular dichroism = different absortpion of LH and RH.

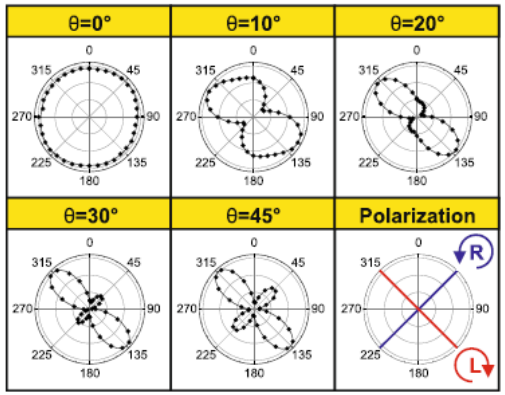


Engineered materials can mimic chiral effects

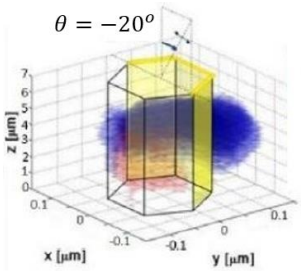
- **Nanophotonics:**

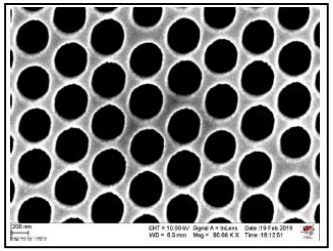
circular polarization light sources and control, chiral field formation and manipulation





- Optics + chemistry, biology: precise discrimination of good/bad entantiomers – enhanced enantioselectivity, even removal





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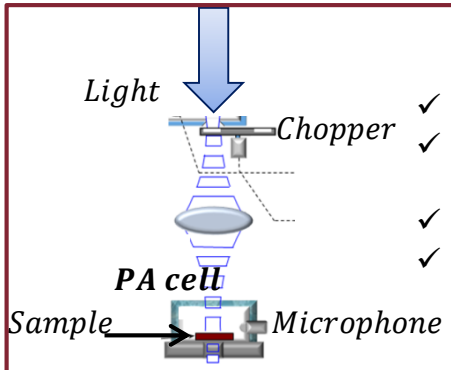

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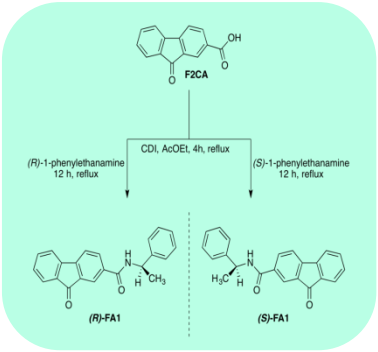

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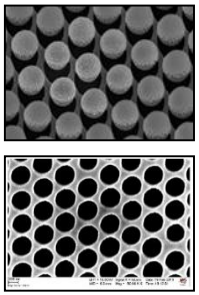

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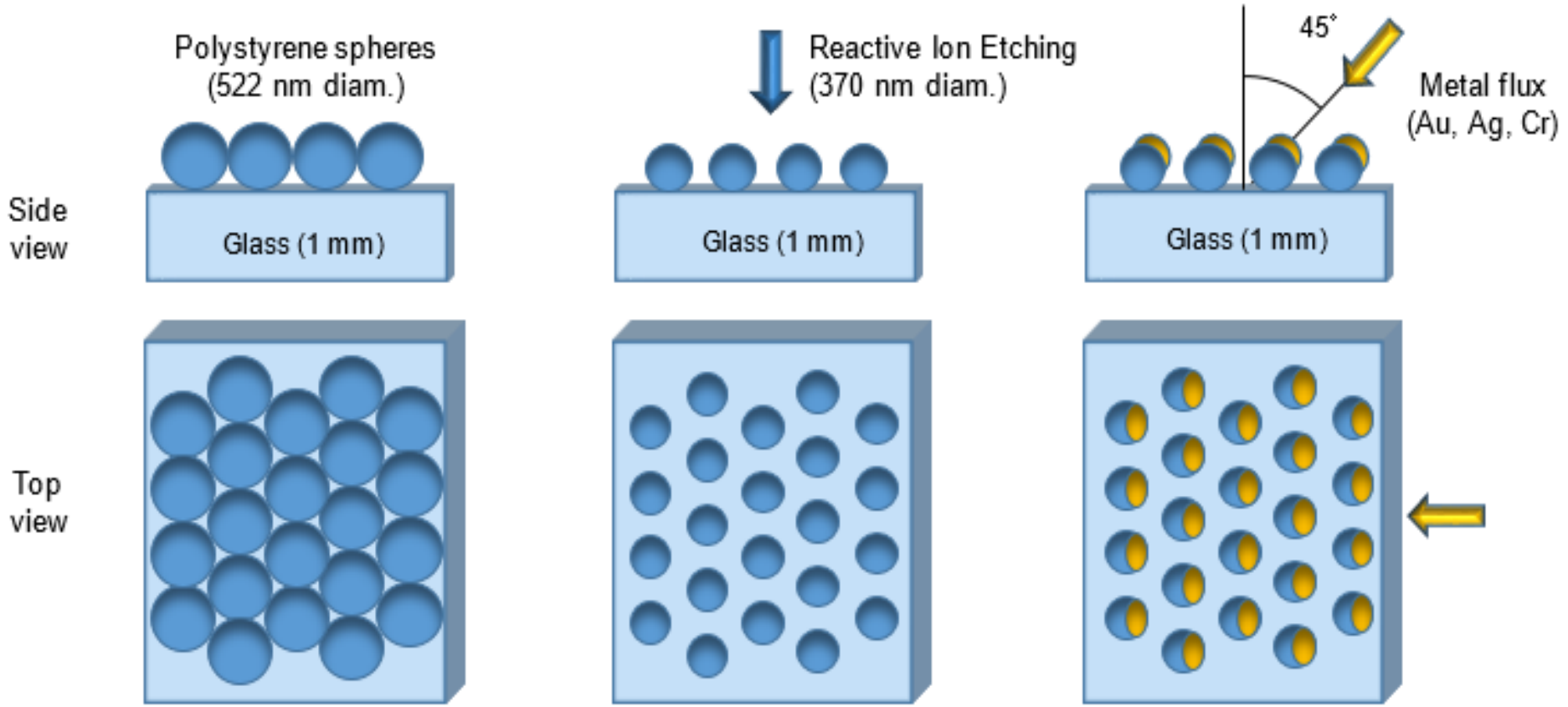
Chiral effects in hybrid metal-polystyrene metasurfaces

Nanosphere lithography

- Commercial polystyrene (PS) nanospheres (MicroParticles GmbH, Germany), D=522nm: self-assembled to form a close-packed monolayer on the soda-lime glass substrates
- RIE to reduce to D=370nm, preserving the 2D ordered arrangement
- Tilted thermal evaporation at 45˚ of Au, Ag or Cr



E. Petronijevic et al, Appl. Phys. Lett. 114 (5), 053101, 2019.

Chiral effects in hybrid metal-polystyrene metasurfaces

SEM images

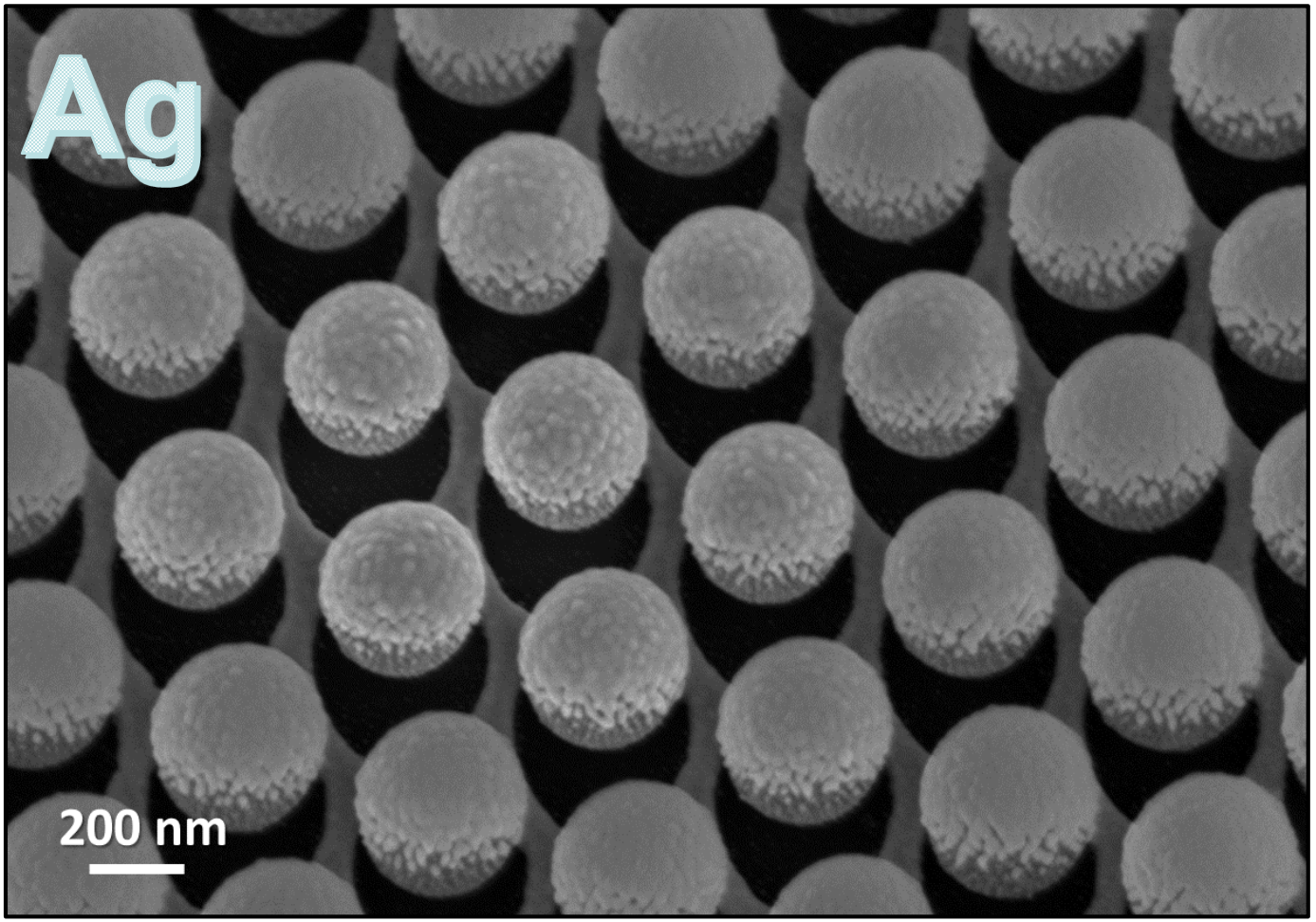
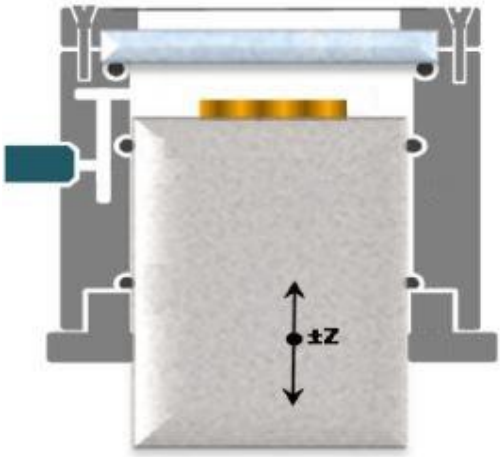
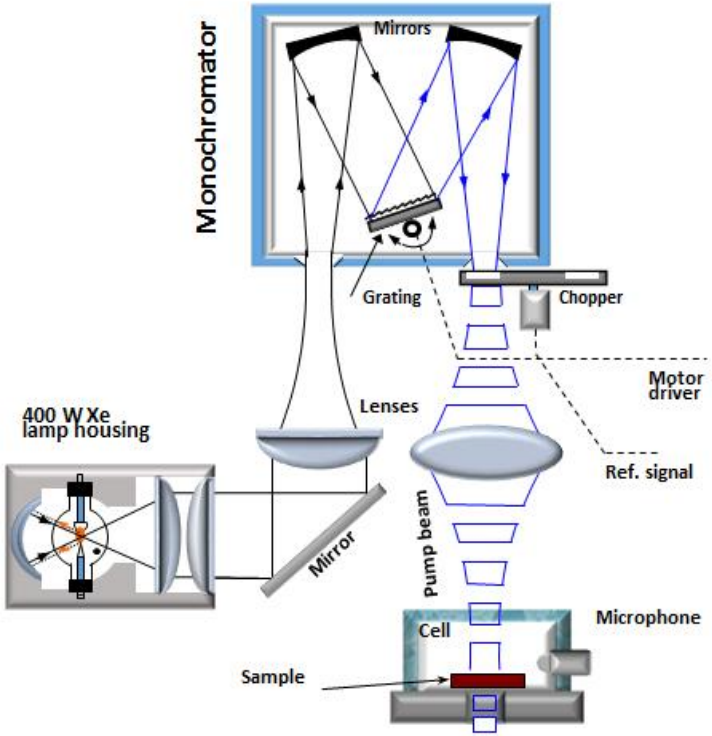


Photo – acoustic technique

- Absorbed light generates heat
- Modulation by a chopper at *f*
- Modulation → cooling/heating cycles
- Pressure changes → acoustic signal caught by mic
- Scattering-independent measurement of absorption



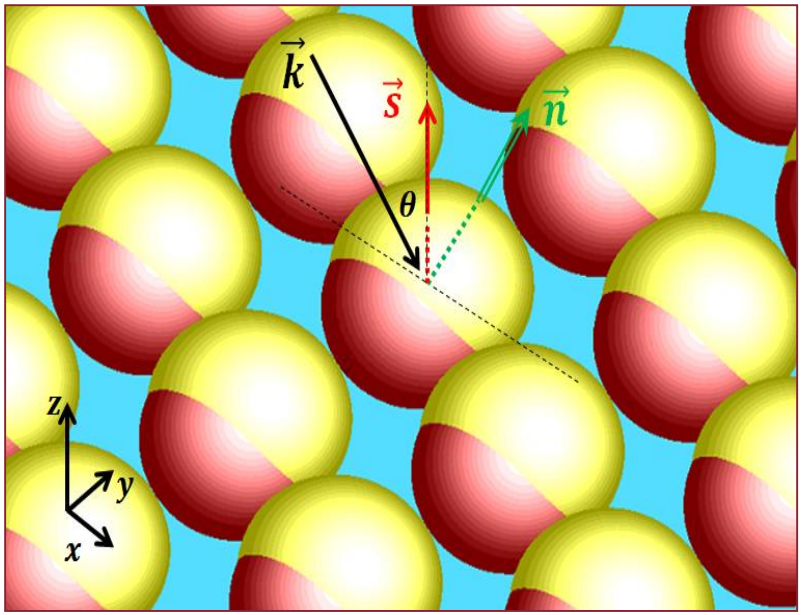


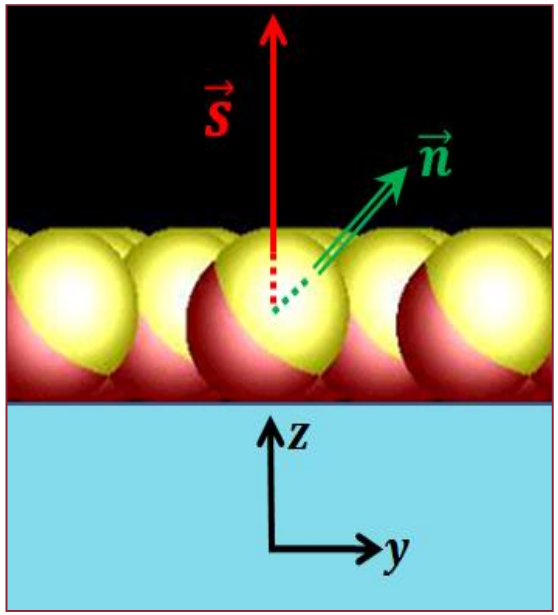
- Grating choice for spectral characterization
- Lasers for focusing and oblique incidence measurements
- Absorption of the nanostructured part of the surface

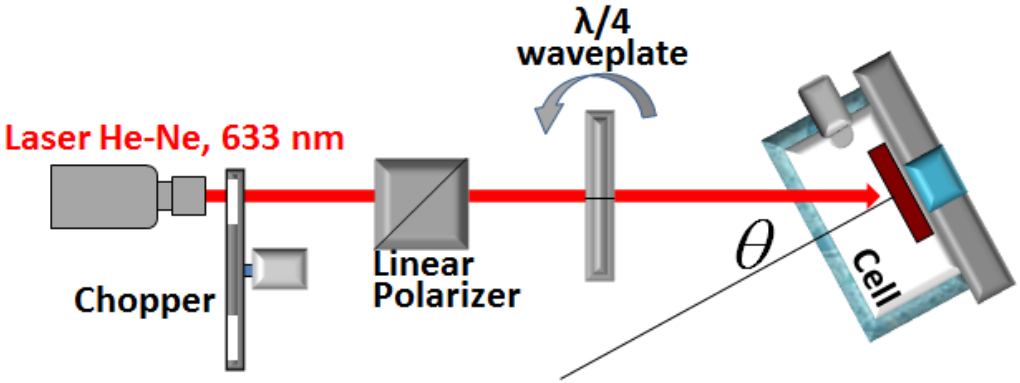
✓ Nondestructive characterization
✓ Scattering-independent
✓ Simple, stable, reliable, low-cost
✓ Directly A – no post-processing needed
✓ Set-up adaptable for angled incidence

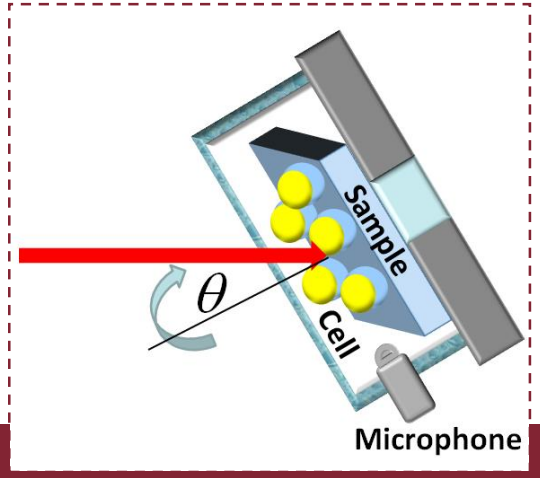
Chiral effects in hybrid metal-polystyrene metasurfaces

- Circular dichroism measurements: PAS difference between LCP and RCP









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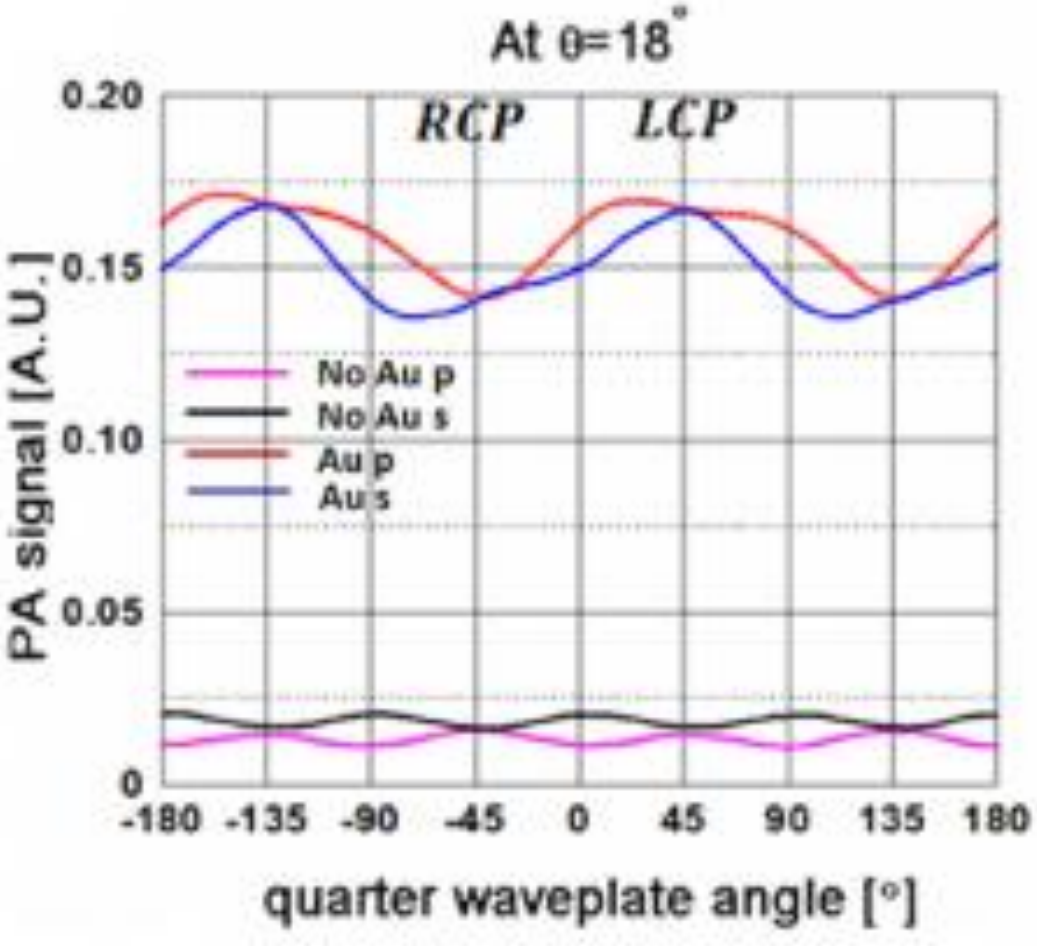

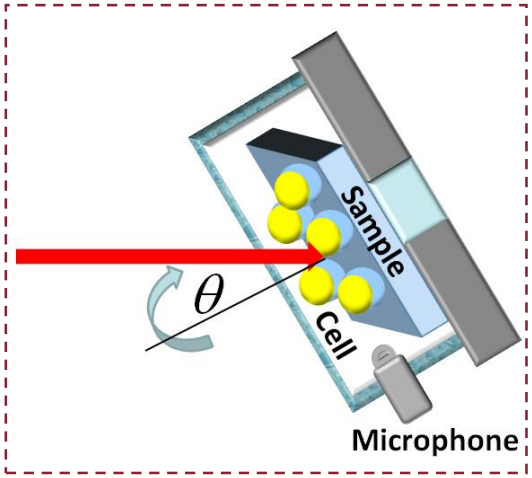

$$CD[\%] = \frac{A_{LCP} - A_{RCP}}{A_{LCP} + A_{RCP}} \cdot 200$$

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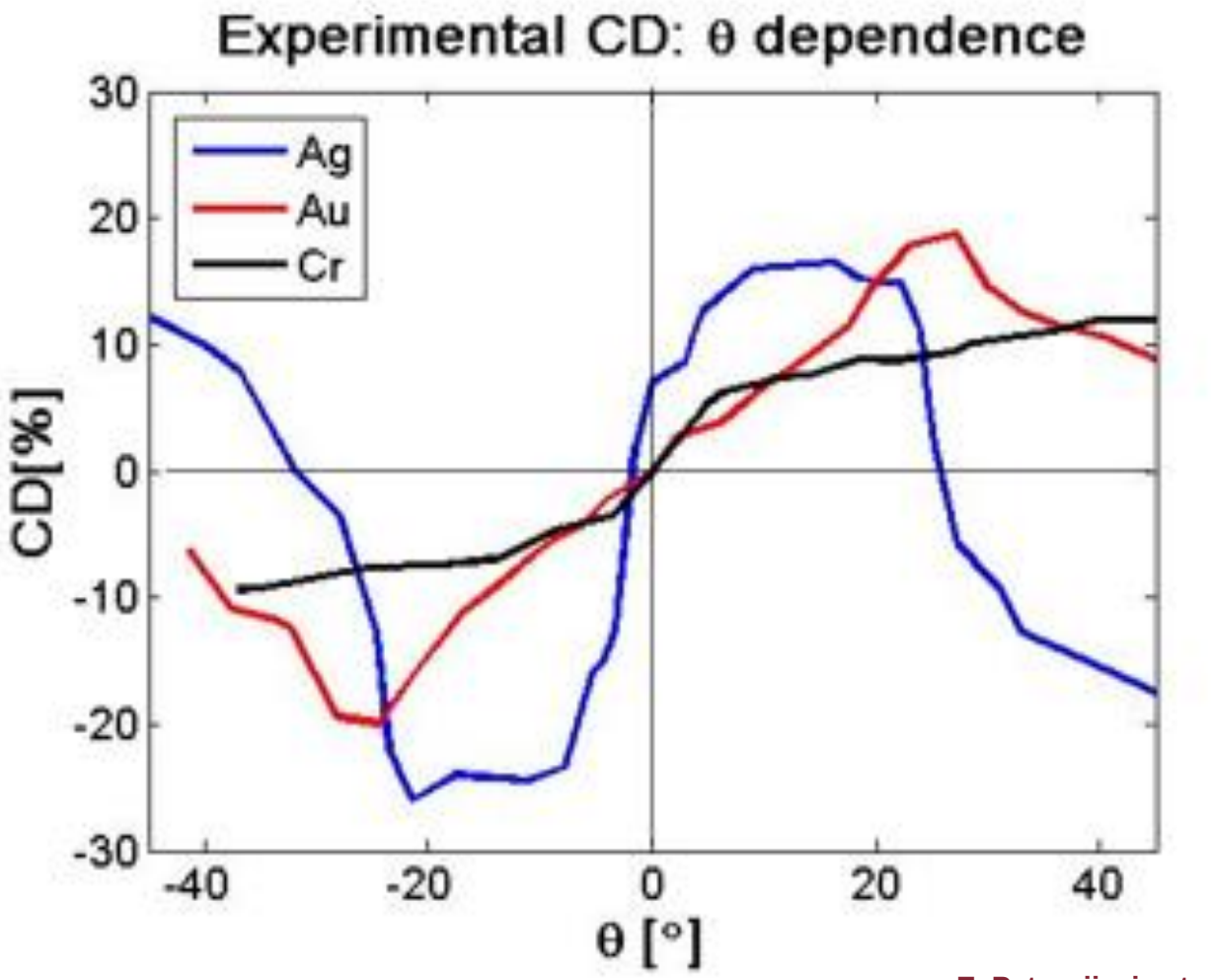

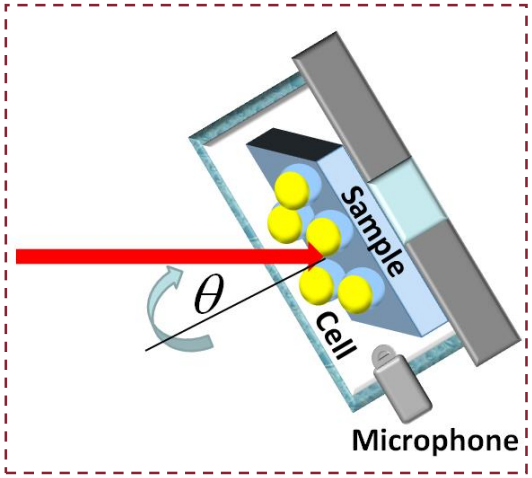

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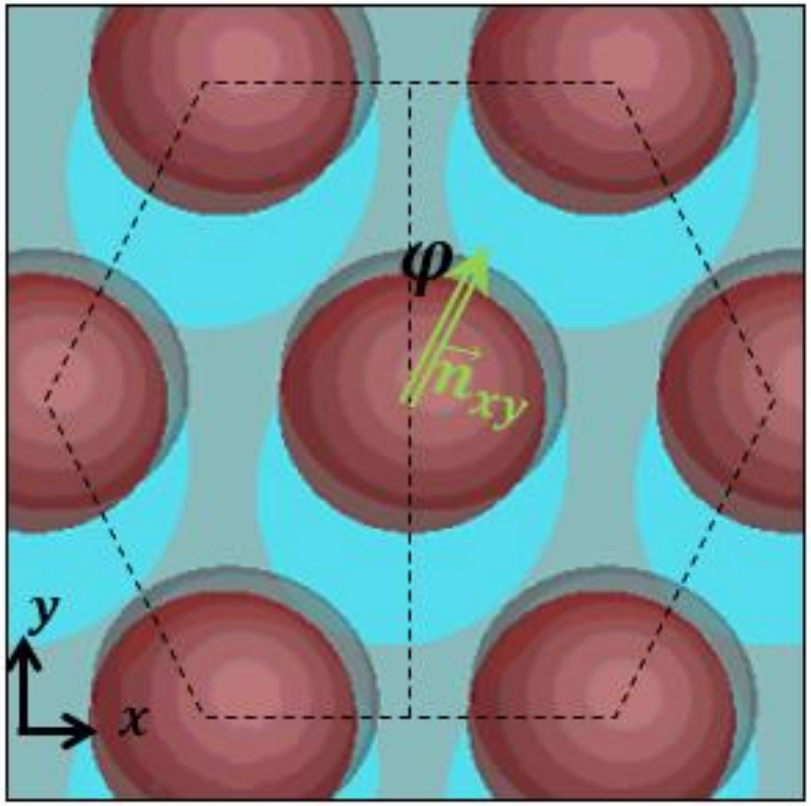
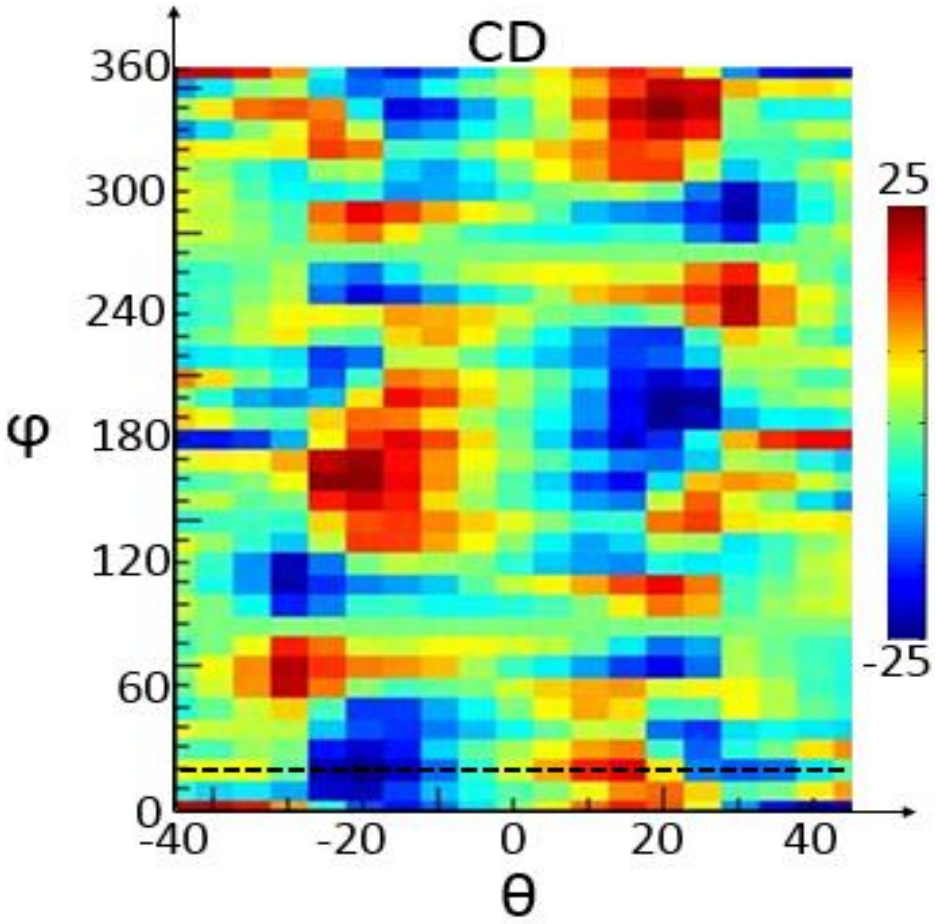
Chiral effects in hybrid metal-polystyrene metasurfaces

- Modelling with the metallic grid on the substrate





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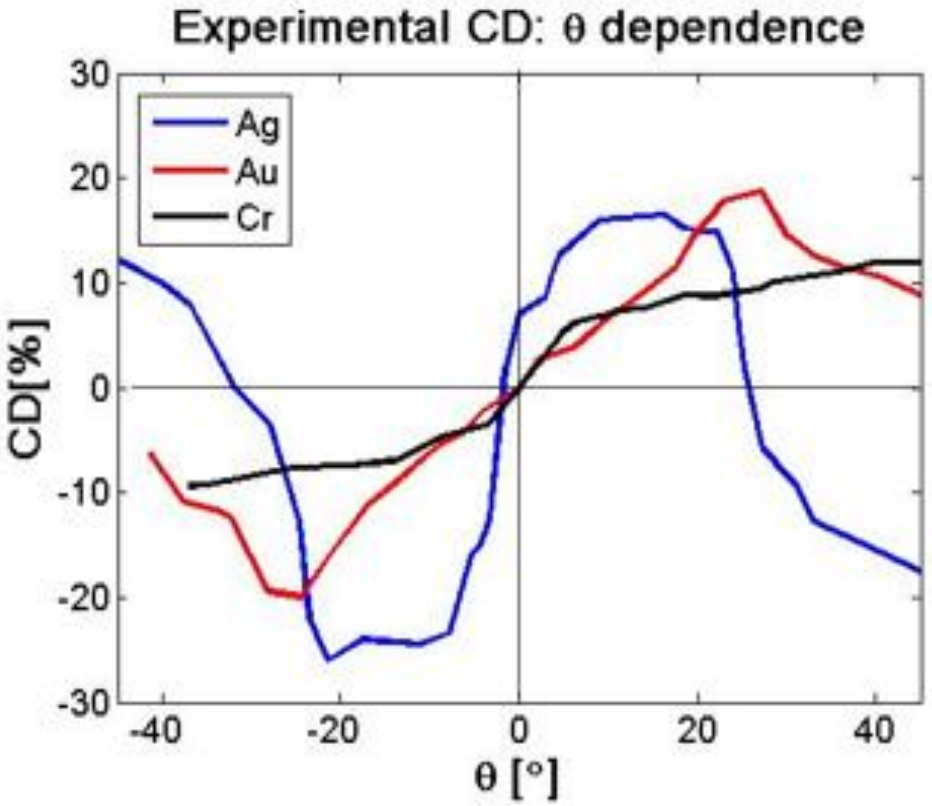
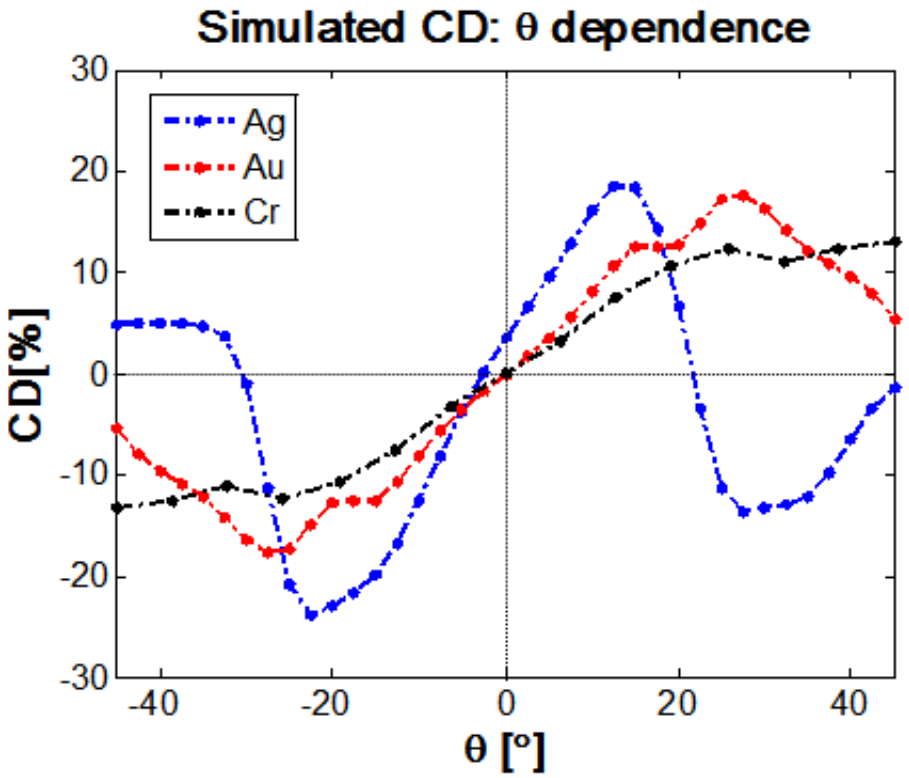
Chiral effects in hybrid metal-polystyrene metasurfaces

- Modelling with the metallic grid on the substrate: φ=20˚





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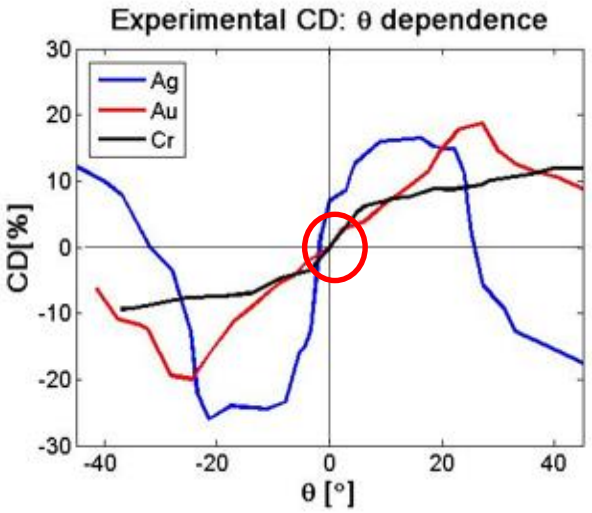
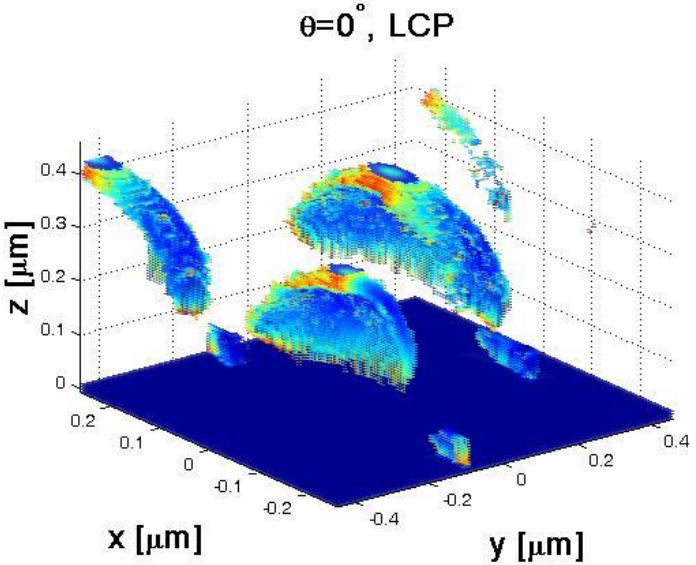
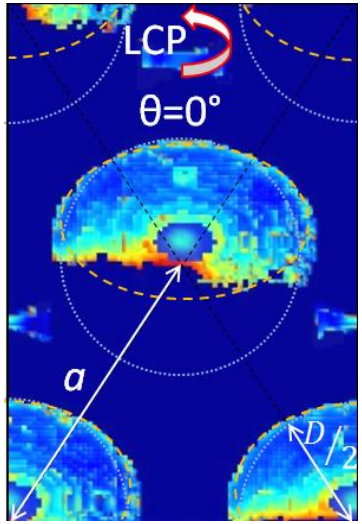
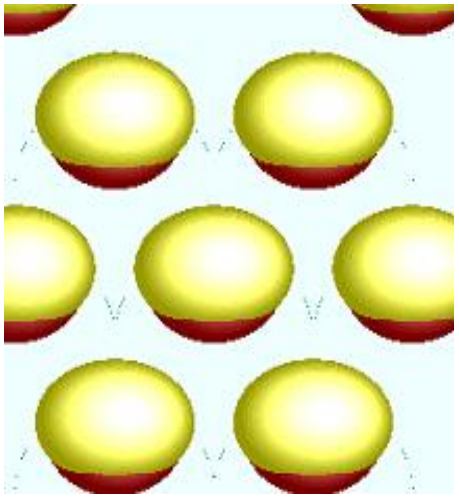
Chiral effects in hybrid metal-polystyrene metasurfaces

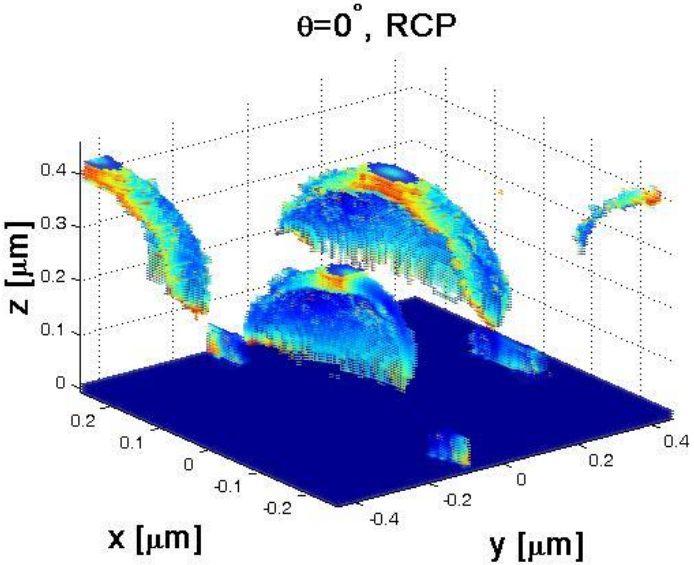
Au

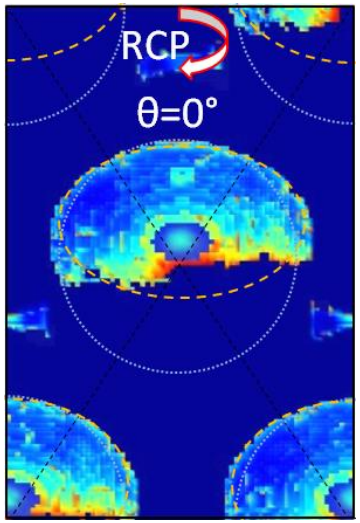












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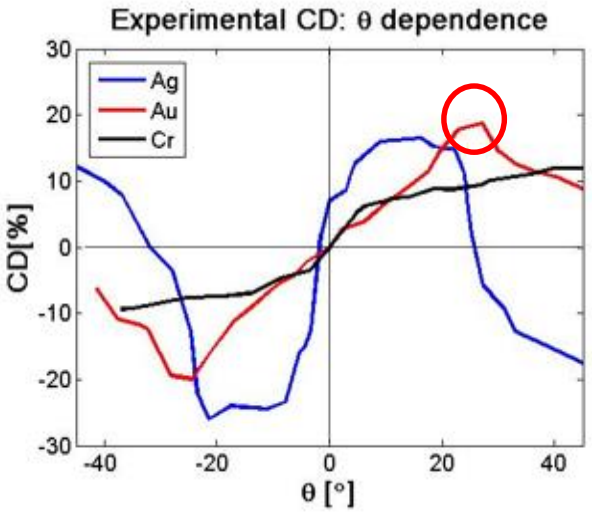

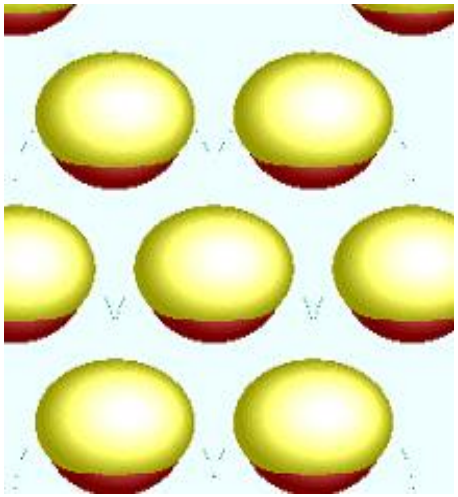

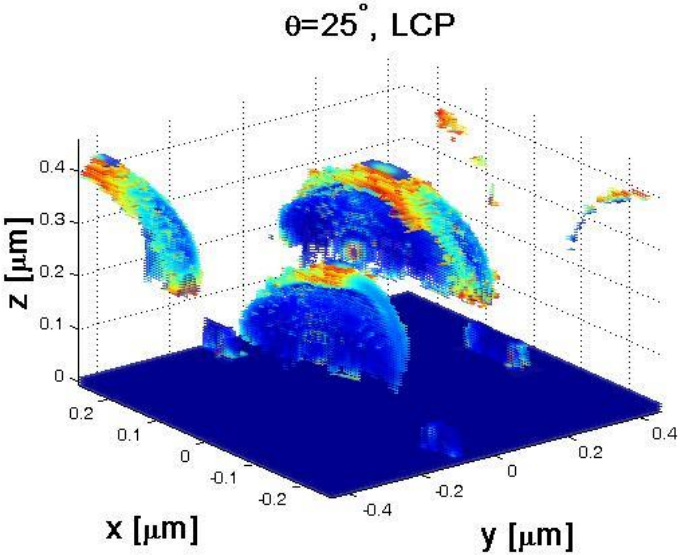

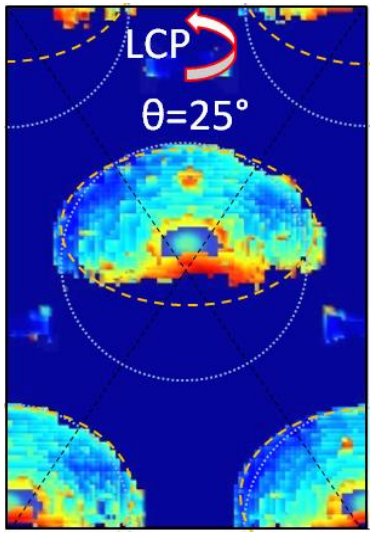

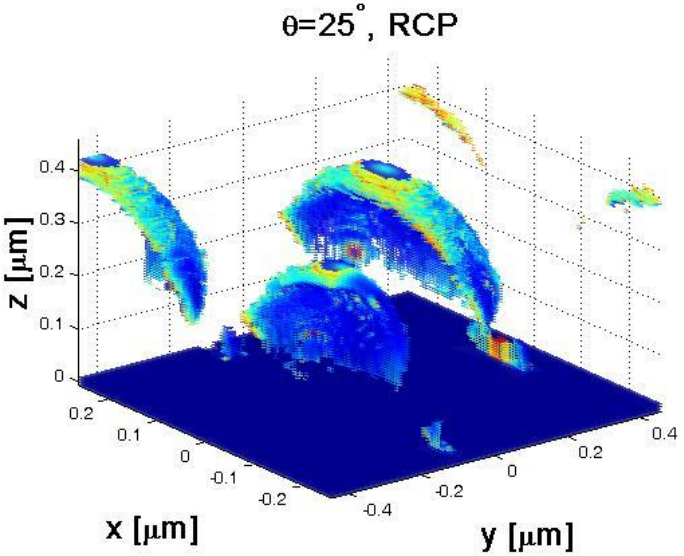

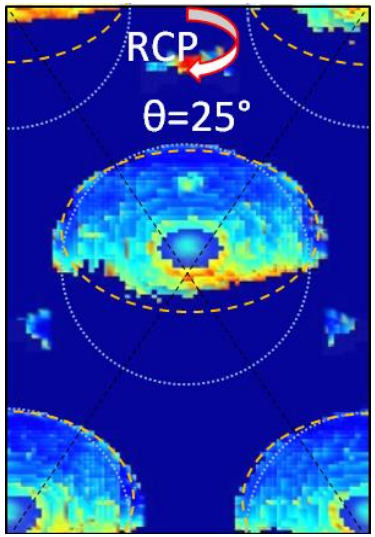

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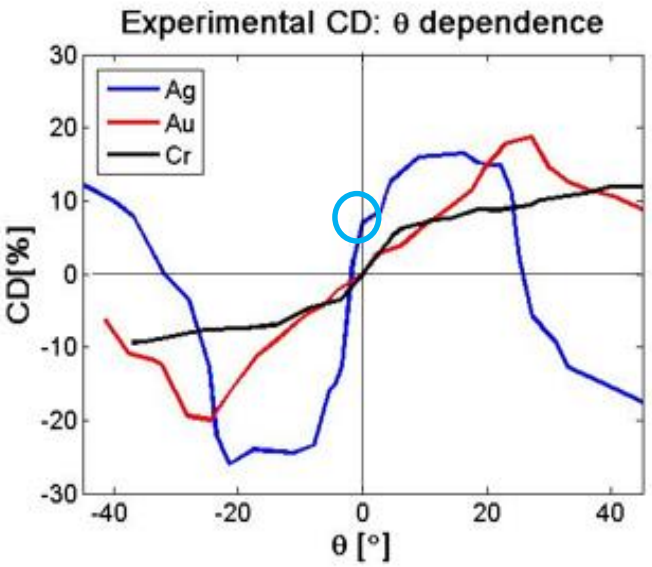
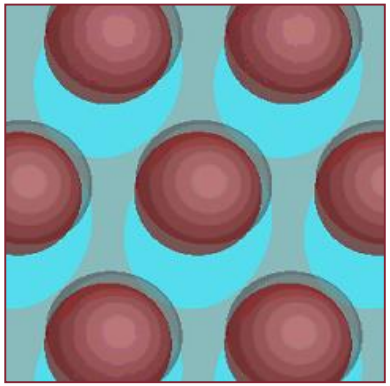
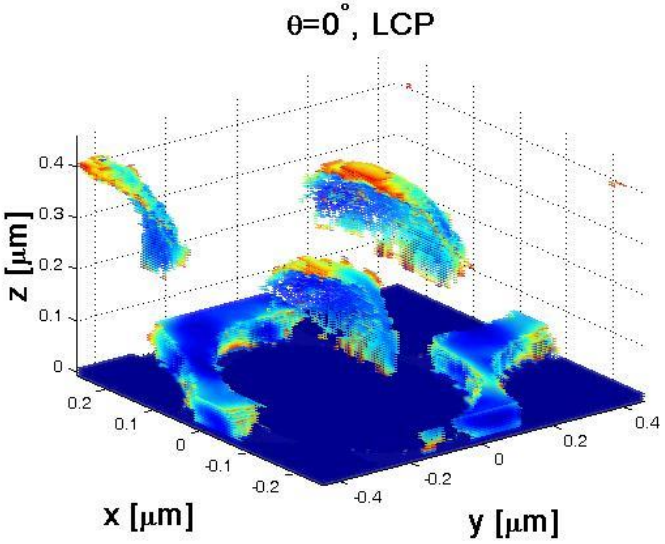
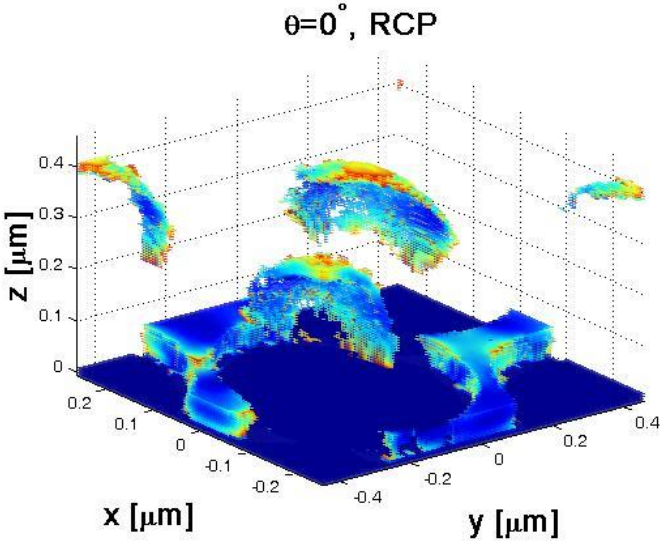
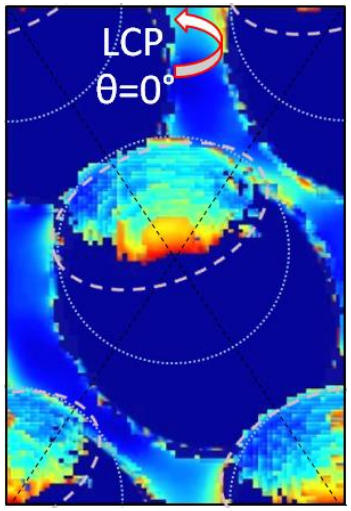
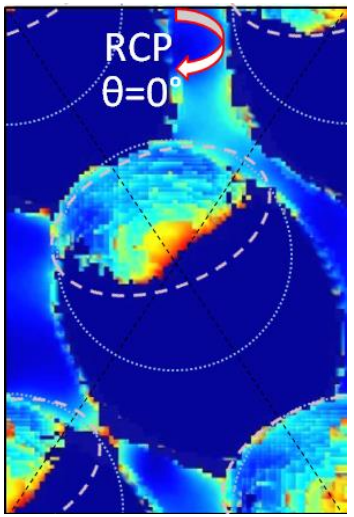




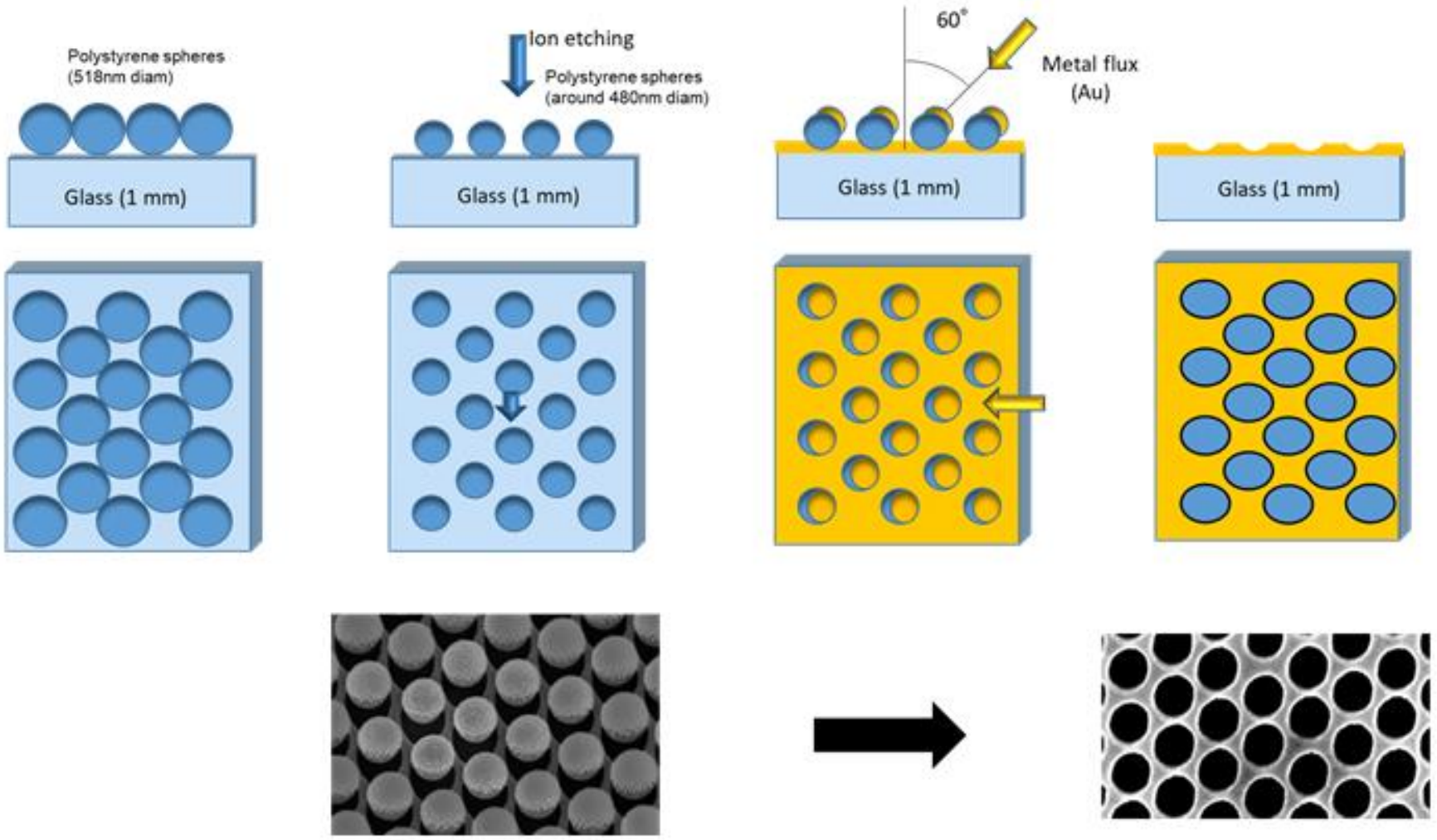






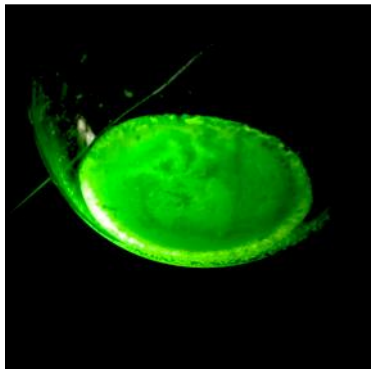


Going more *planar*

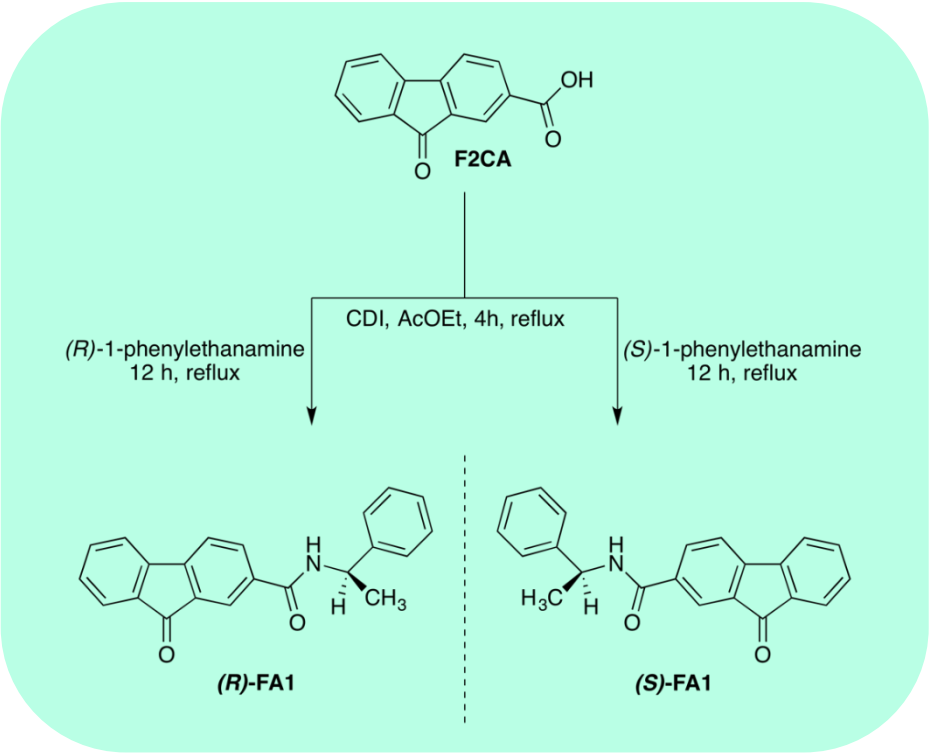


Going more *planar*

- The two enantiomers: (R) – FA1 and (S) – FA1



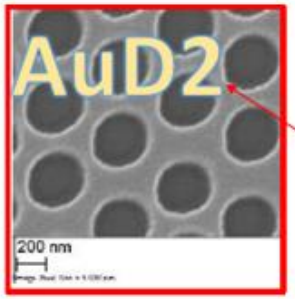
***(R)*-FA1** in the solid state
UV light at 365 nm

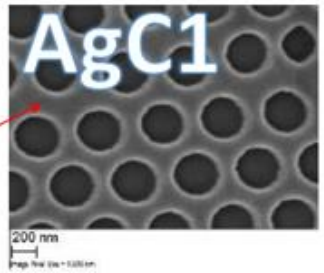


DMF Solutions of
***(R)*-FA1** (right) and ***(S)*-FA1** (left)
Daylight and UV light at 365 nm

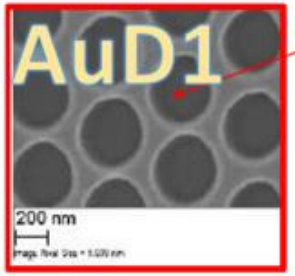
Going more *planar*

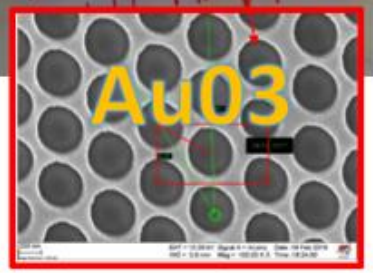
Samples Padova – elliptic nanoholes

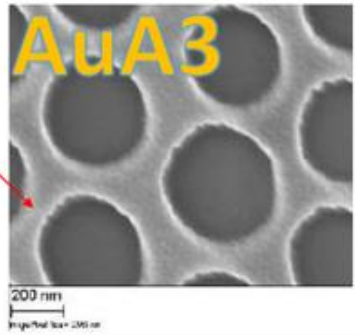




$$Ext_{-45} = 1 - T_{-45}$$
$$Ext_{45} = 1 - T_{45}$$
$$CD[\%] = 100\frac{Ext_{-45} - Ext_{45}}{Ext_{-45} + Ext_{45}}$$

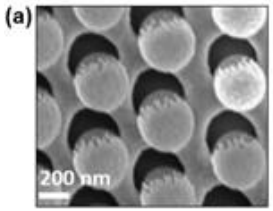


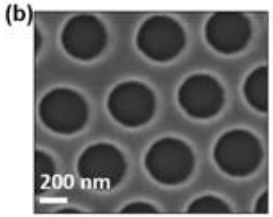


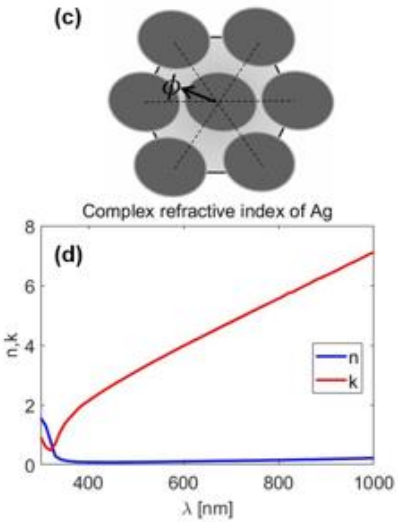


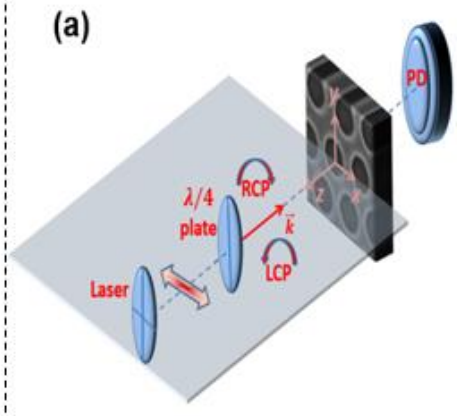
Going more *planar*

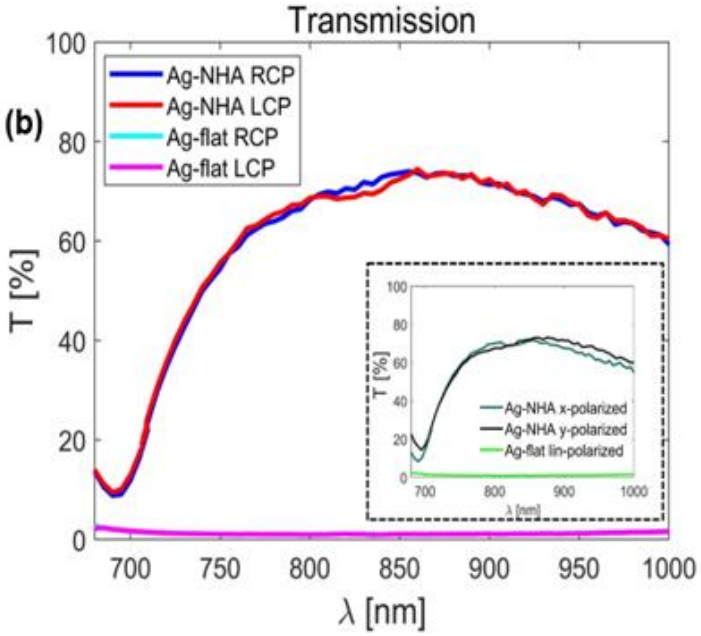
Sample AgC1



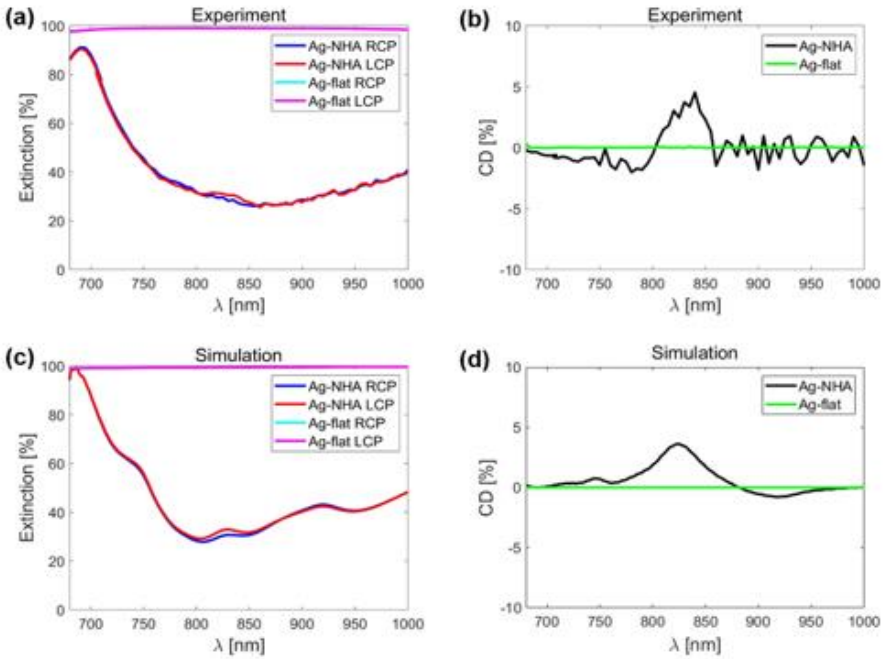


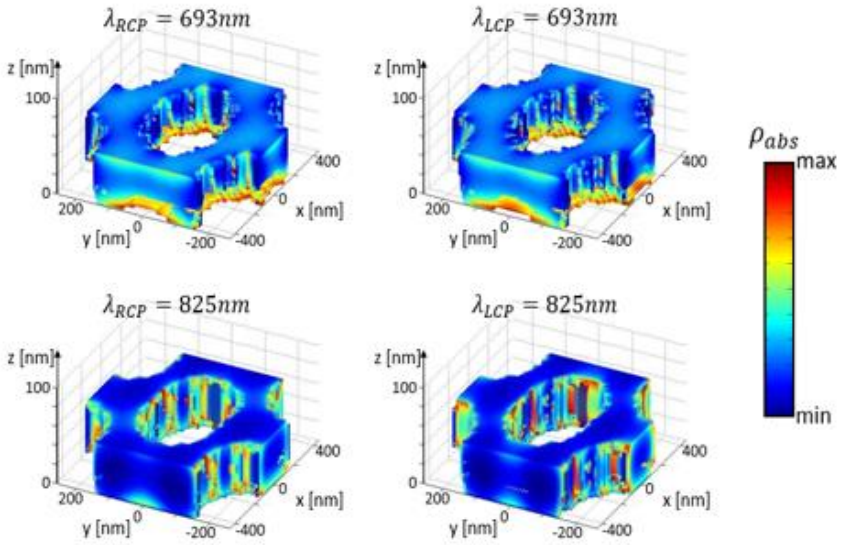






Sample AgC1





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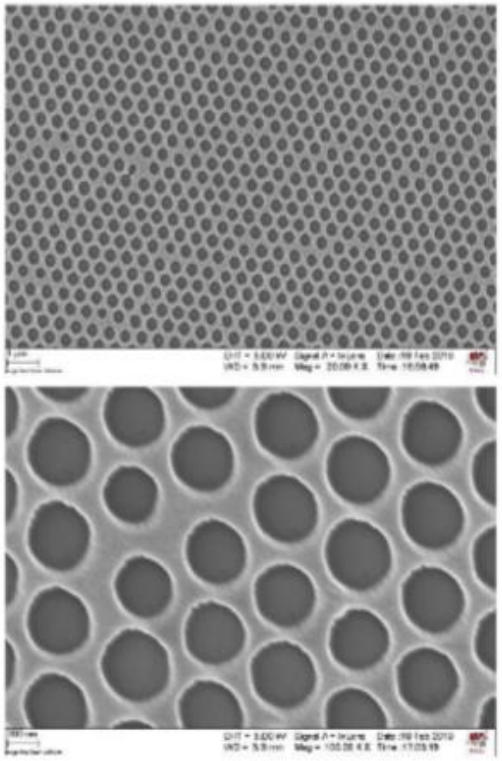
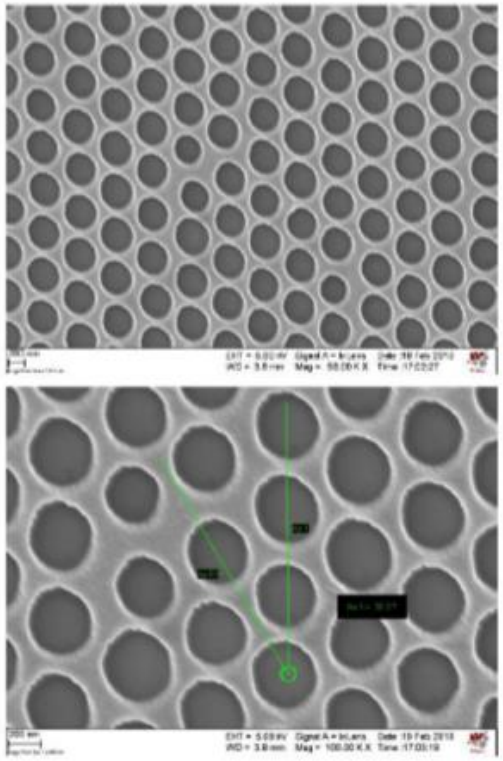
Going more *planar*

Sample AuA3

A3: A_SLG-PS518_RIE929_EVA359 Au 52 nm tilt 45°+ in-plane 28°

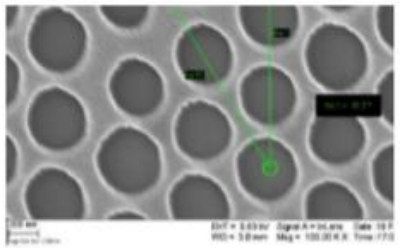




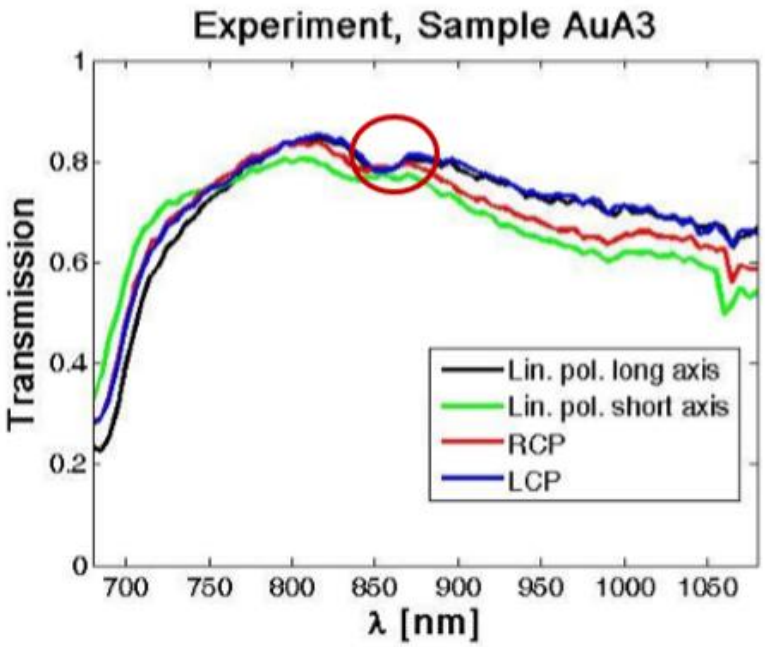
Going more *planar*

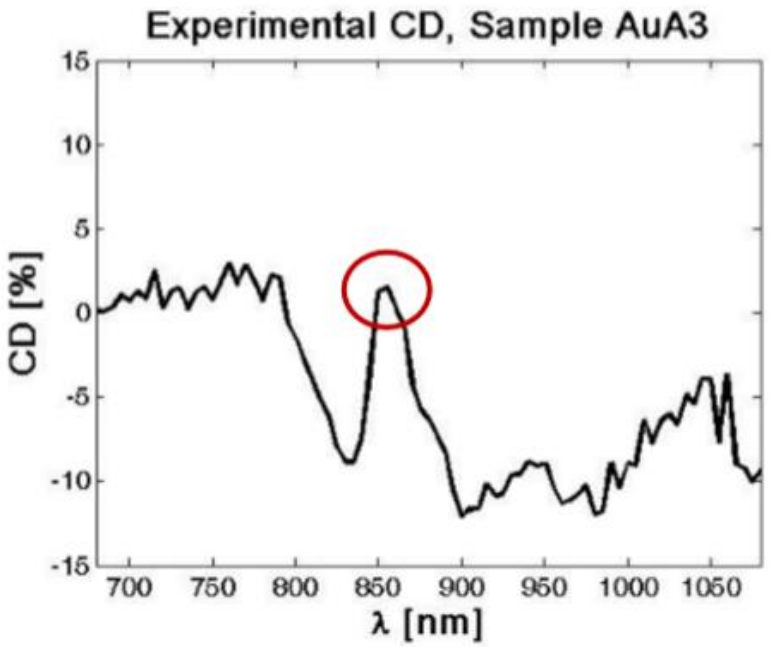
Sample AuA3

$ND = 1.0$



≈chiral



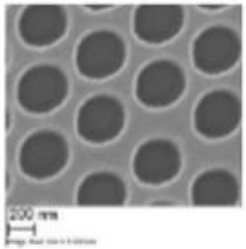


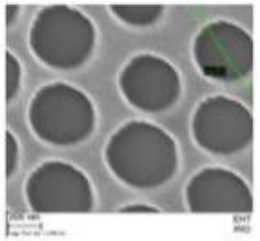
Going more *planar*

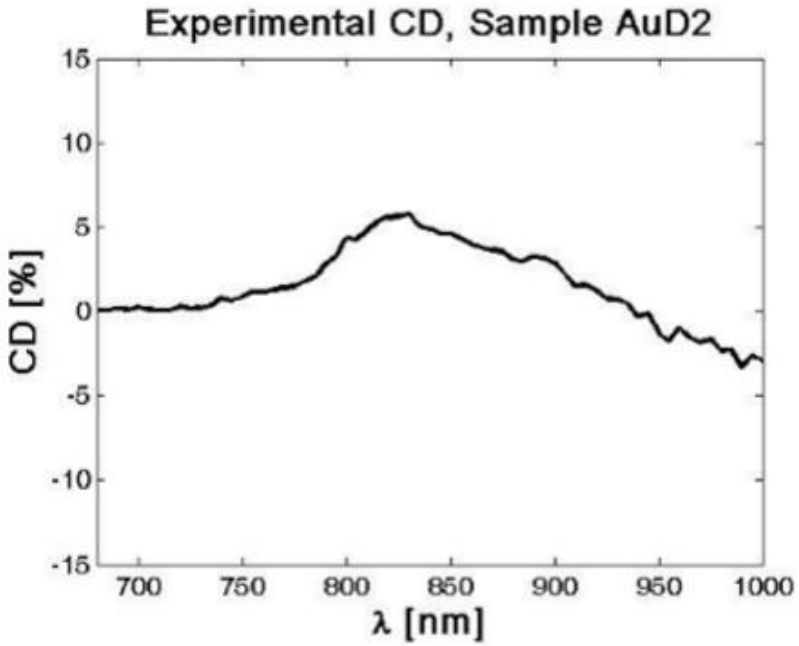
Sample AuD2

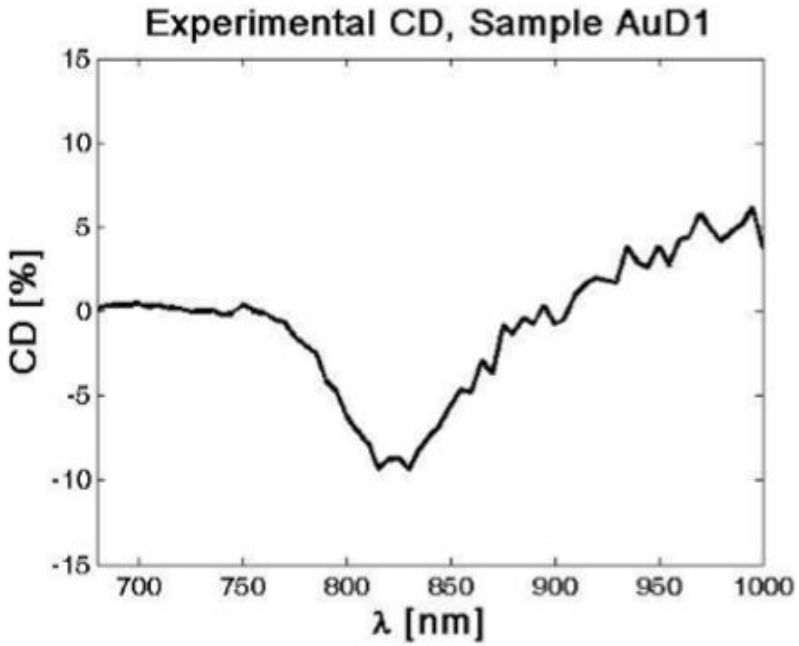
$ND = 1.0$

Sample AuD1



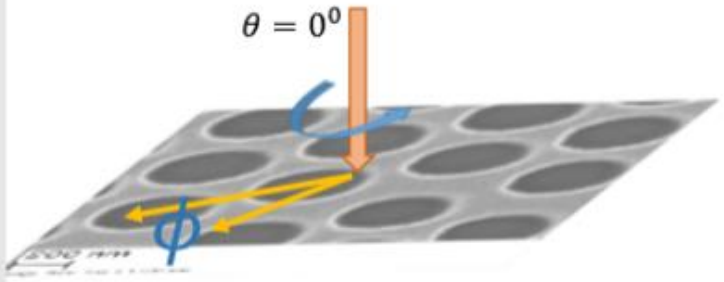






Going more *planar*

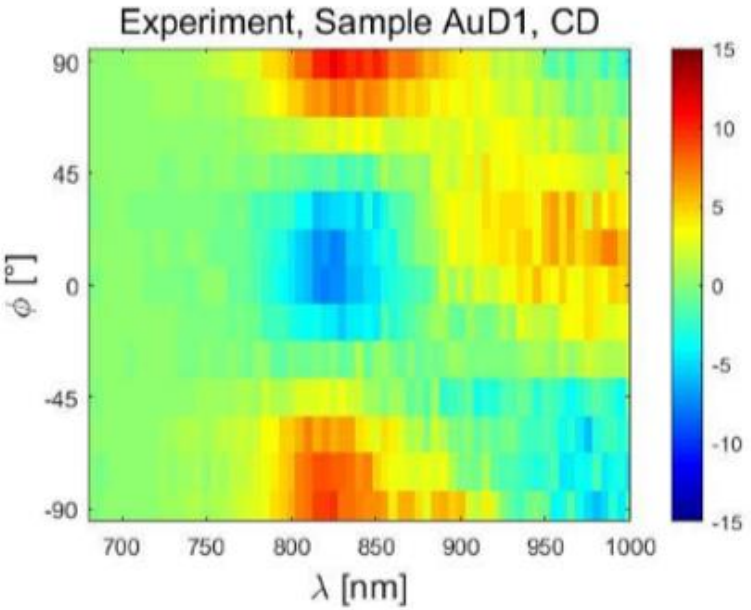
Experiment: in-plane rotation, normal incidence

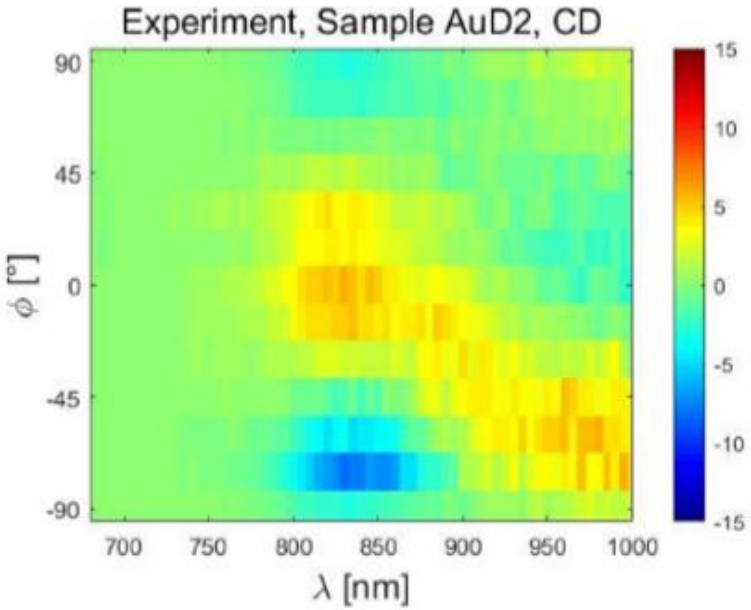


$$Ext_{-45} = 1 - T_{00,-45}$$

$$Ext_{45} = 1 - T_{00,45}$$

$$CD[\%] = 100\frac{Ext_{-45} - Ext_{45}}{Ext_{-45} + Ext_{45}}$$

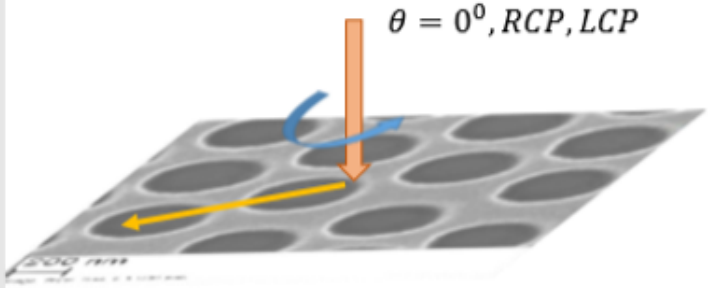


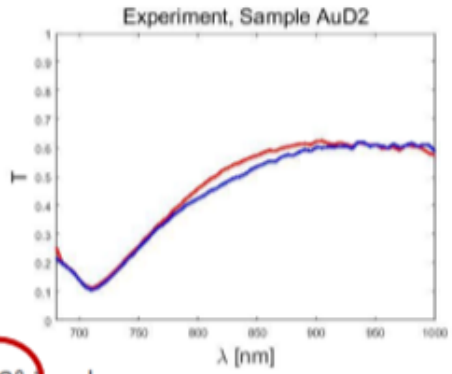


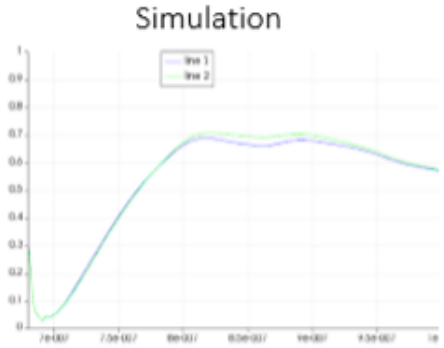
Going more *planar*

Simulations: elliptical nanoholes

$\theta = 0^0, RCP, LCP$

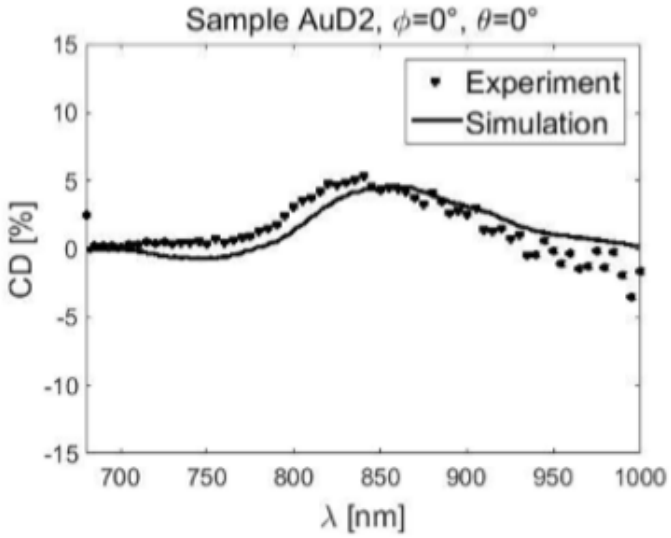






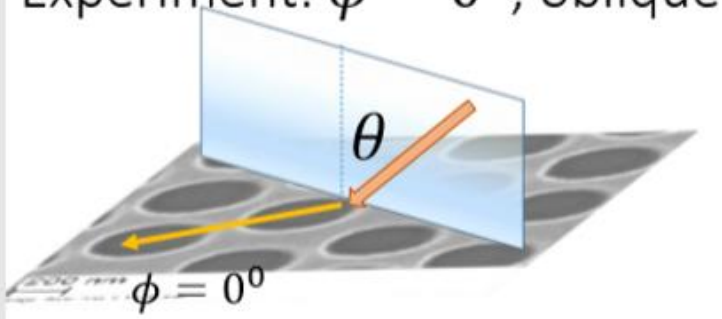
D_SLG-PS518_RIE928_EVA357 Ag/Au 9+43 nm tilt 45° + 28° in-plane

(tilt angle 152=180-28)

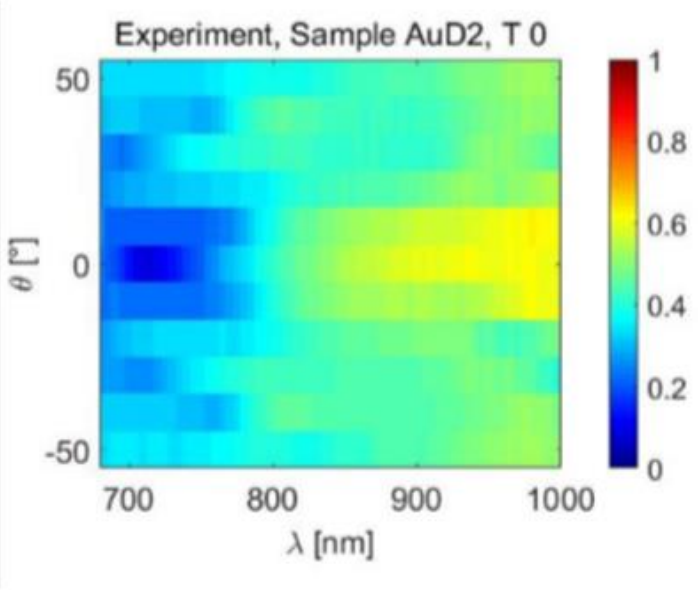


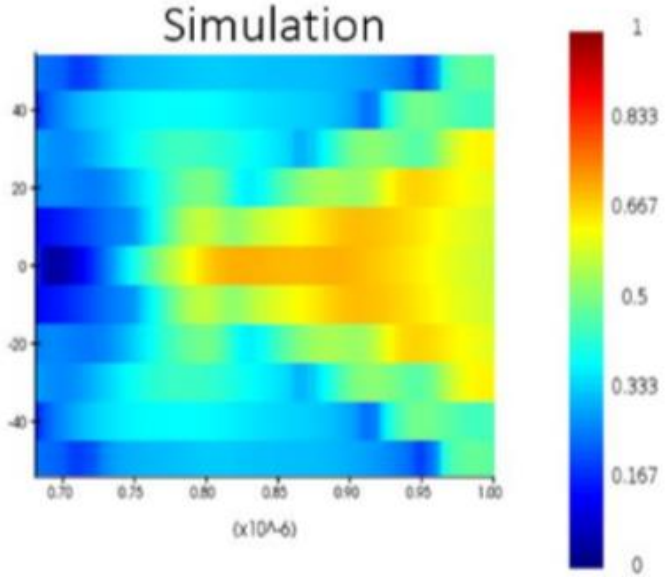
Going more *planar*

Experiment: $\phi = 0^0$, oblique incidence



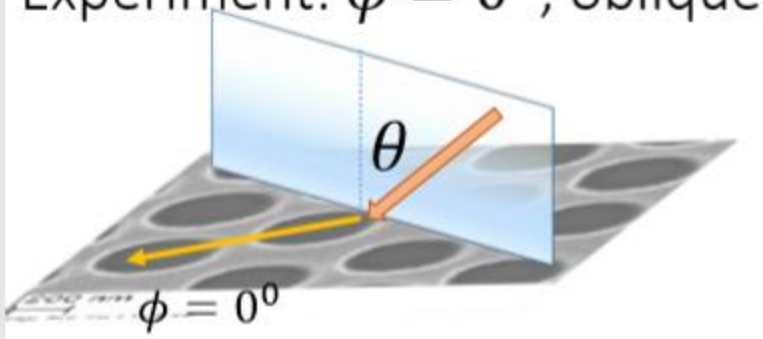
$$\lambda = \frac{P}{\sqrt{\frac{4}{3}(i^2 + ij + j^2)}} \left(\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} - \eta_D \sin\theta \right)$$

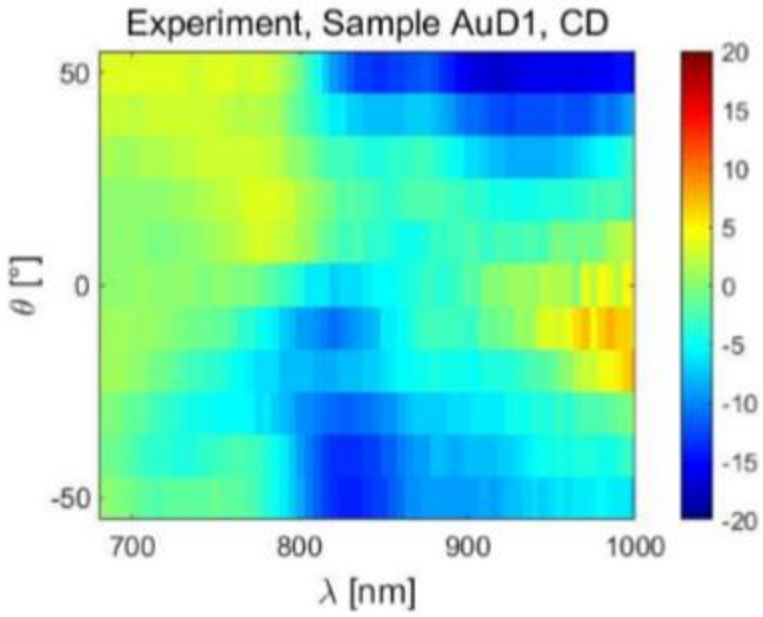


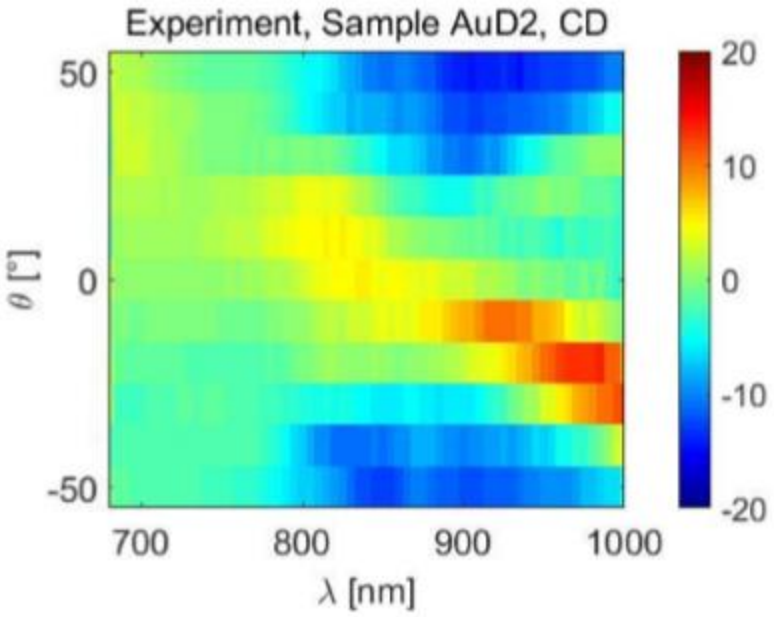


Going more *planar*

Experiment: $\phi = 0^0$, oblique incidence

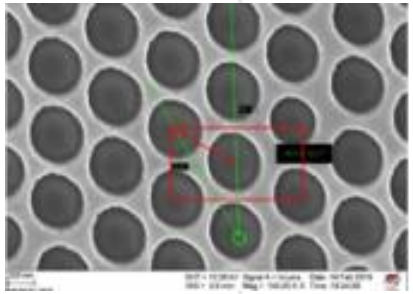


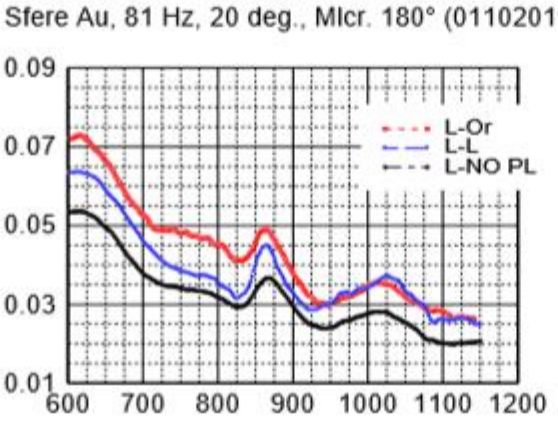


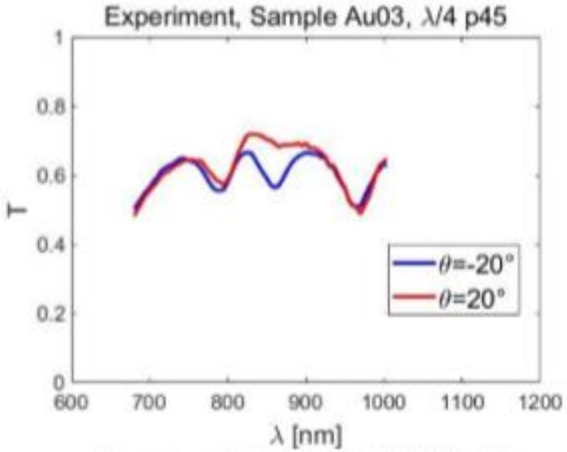


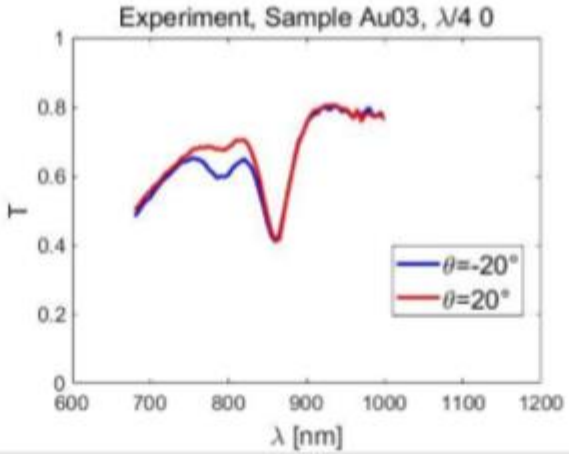
Sample Au03

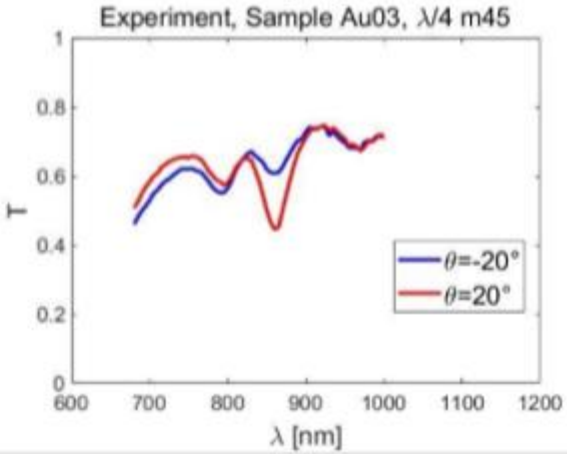
$|\theta| = 20°$



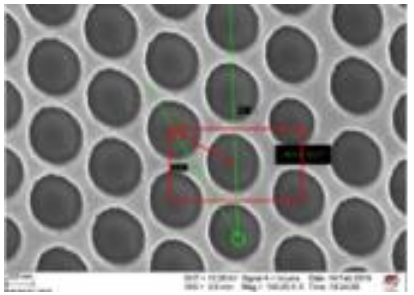


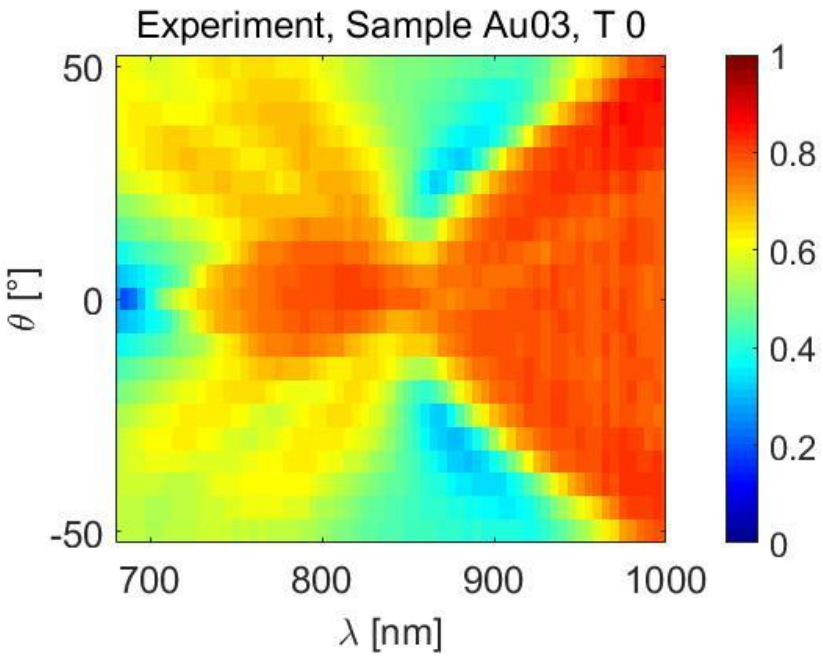


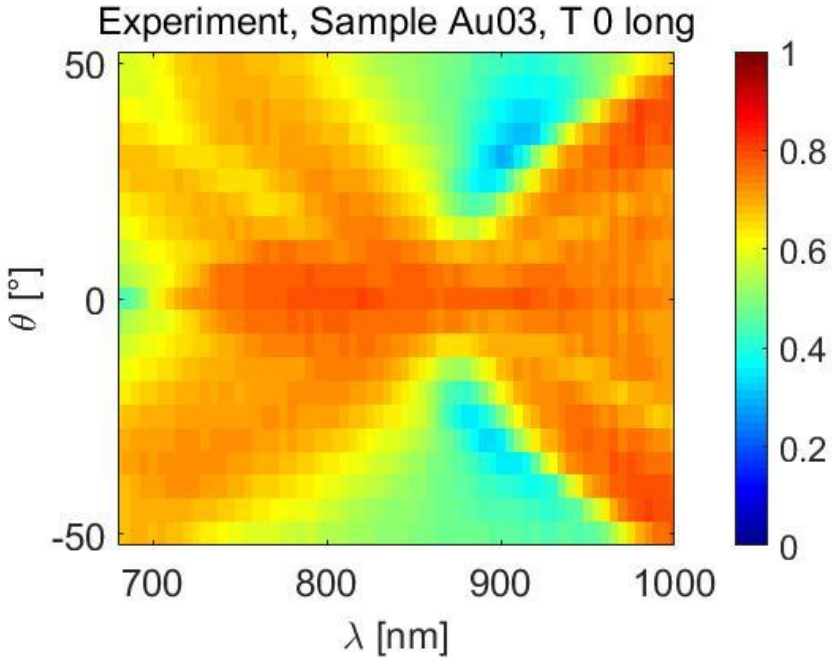




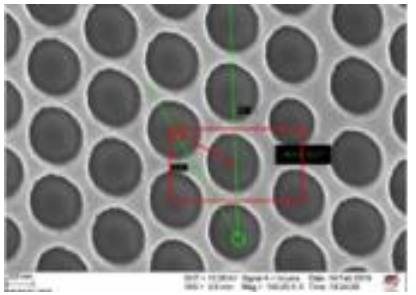
Sample Au03

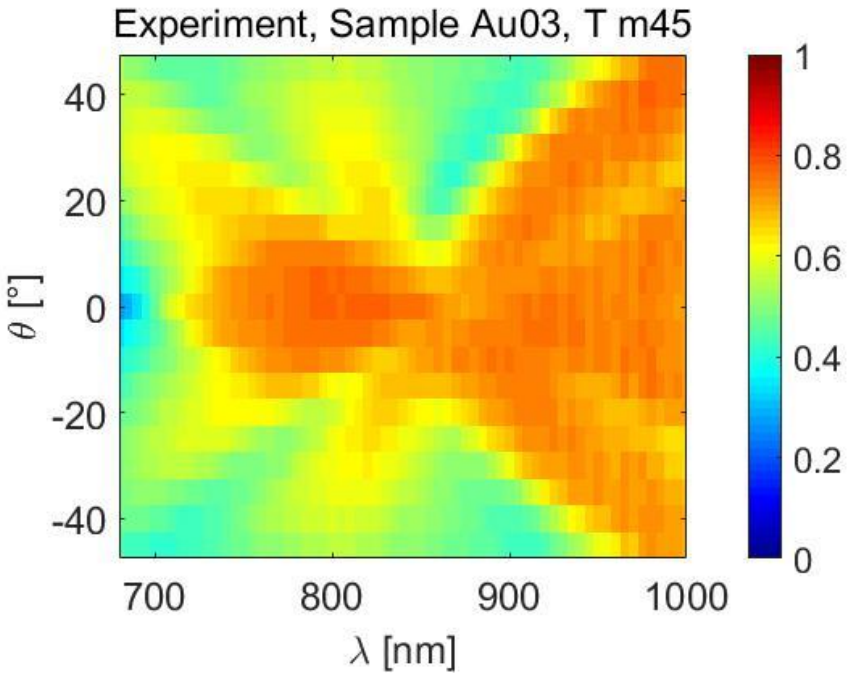


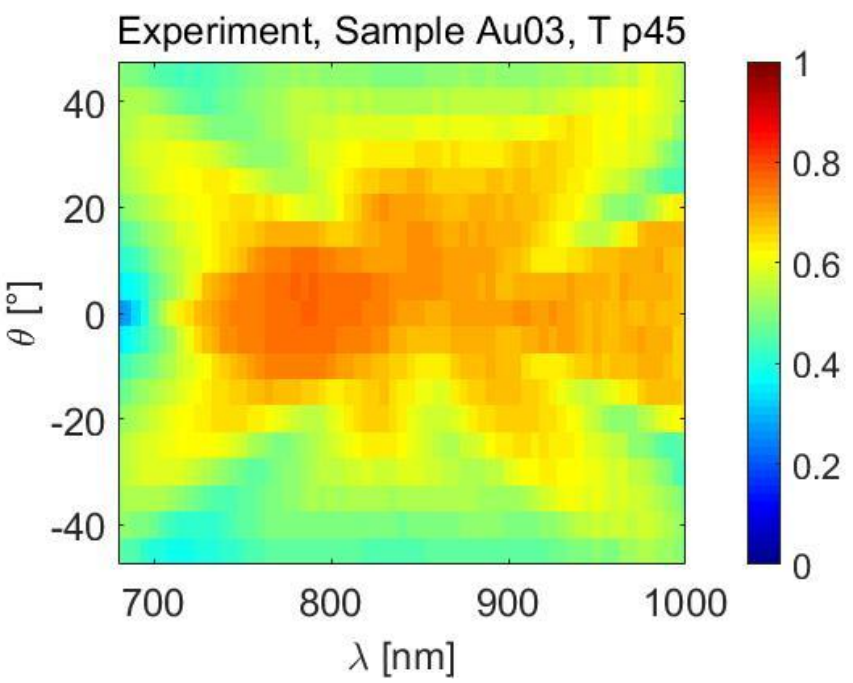

Experiment, Sample Au03, T 0
50
0
-50
θ [°]
700
800
900
1000
λ [nm]
1
0.8
0.6
0.4
0.2
0


Experiment, Sample Au03, T 0 long
50
0
-50
θ [°]
700
800
900
1000
λ [nm]
1
0.8
0.6
0.4
0.2
0

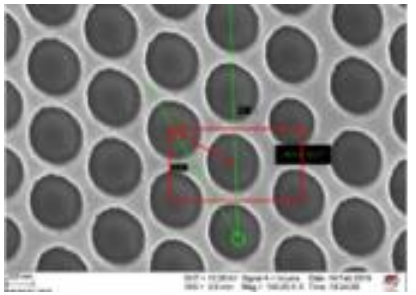
Sample Au03

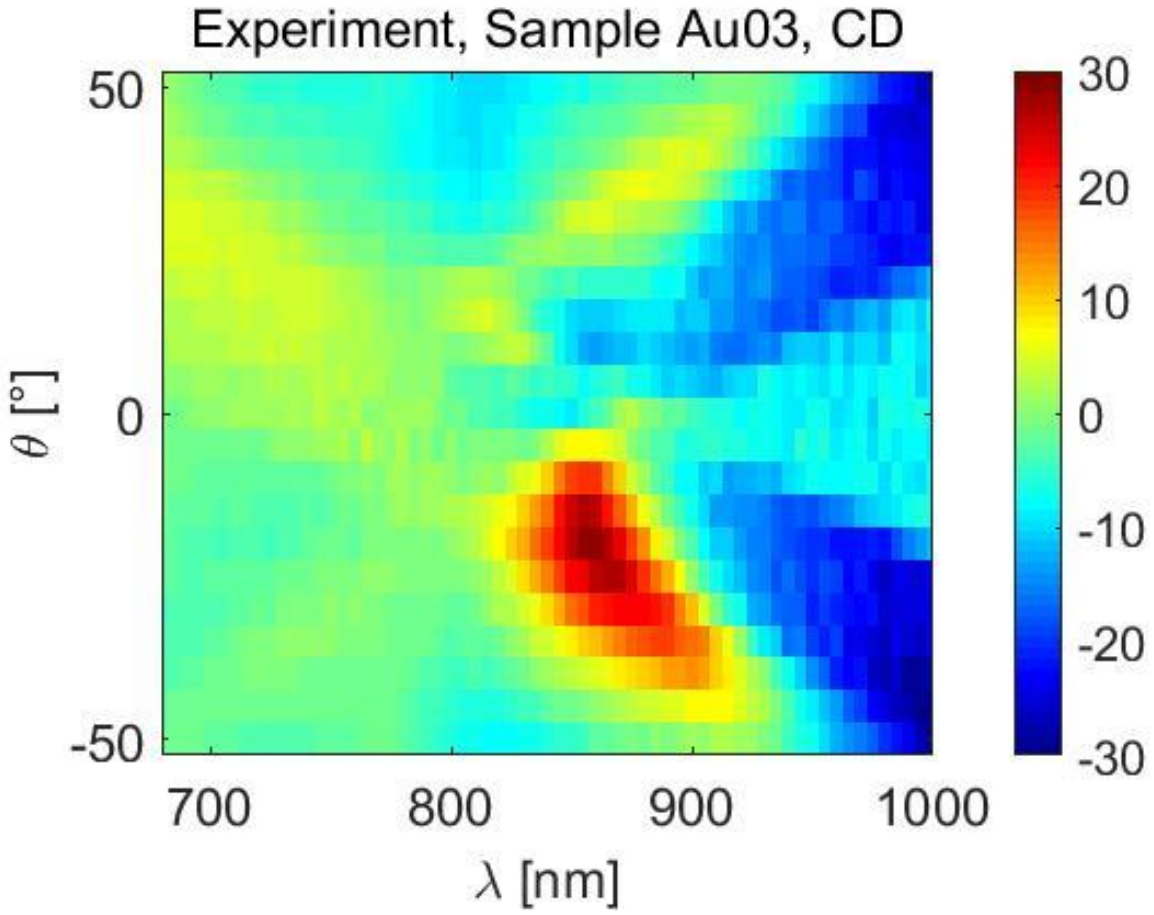



Experiment, Sample Au03, T m45
40
20
0
-20
-40
θ [°]
700
800
900
1000
λ [nm]
1
0.8
0.6
0.4
0.2
0


Experiment, Sample Au03, T p45
40
20
0
-20
-40
θ [°]
700
800
900
1000
λ [nm]
1
0.8
0.6
0.4
0.2
0

Sample Au03

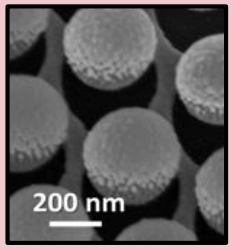


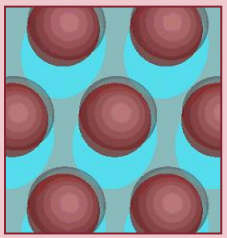

Experiment, Sample Au03, CD
50
0
-50
θ [°]
700
800
900
1000
λ [nm]
30
20
10
0
-10
-20
-30

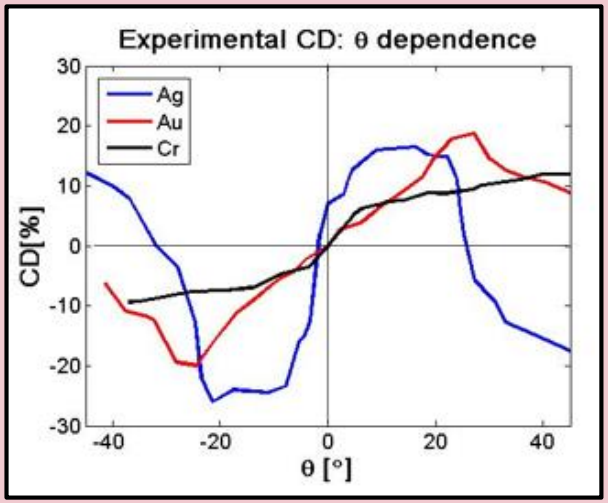
Conclusion

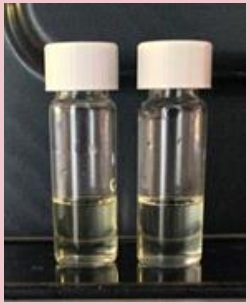
- Nanosphere lithography for low-cost fabrication of high quality plasmonic samples
- Tilting during the fabrication breaks the sample symmetry
- Chiral effects measured in both nanoshell and nanohole samples
- Coupling with chiral molecules for enhanced enantioselectivity

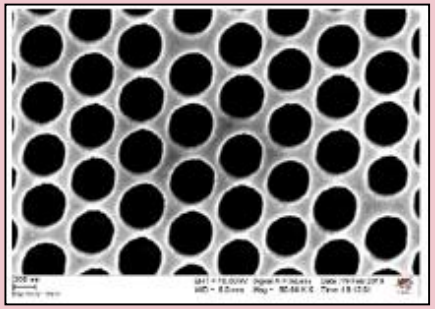
- First results: Despite the very small volume of molecules on the substrate, that give a very low CD at zero degrees of incidence, we can observe boost of the enantioselectivity at larger angles where extrinsic chirality is active.











…to be continued

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The End

That's All Folks!!!!