Chirality in low-cost plasmonics

• Emilija Petronijevic¹, Alessandro Belardini¹, Grigore Leahu¹, Grigore Leahu¹, Fabiana Pandolfi¹, Leonardo Mattiello¹, Tiziana Cesca², Carlo Scian², Giovanni Mattei², and Concita Sibilia¹

1. Sapienza Università di Roma, Dipartimento SBAI, Roma, Italy
2. Università di Padova, Dipartimento di Fisica e Astronomia, Padova, Italy

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

@SBAI
- Synthesis of chiral molecules

In collaboration with:
T. Cesca, C. Scian, N. Michieli, G. Mattei

Physics and Astronomy Department, University of Padova, Padova, Italy.
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.

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

Enantiomers

(a) Chiral objects

(b) Achiral objects

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The simplest chiral system: a triad of nonplanar vectors

Motivation to study chirality

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 absorbption of LH and RH.

Chiral medium

Engineering 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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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


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Chiral effects in hybrid metal-polystyrene metasurfaces

SEM images

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Chiral effects in hybrid metal-polystyrene metasurfaces

**Photo – acoustic technique**

- Absorbed light generates heat
- Modulation by a chopper at $f$
- Modulation $\rightarrow$ cooling/heating cycles
- Pressure changes $\rightarrow$ 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
Chiral effects in hybrid metal-polystyrene metasurfaces

- Circular dichroism measurements: PAS difference between LCP and RCP

\[ CD[\%] = \frac{A_{LCP} - A_{RCP}}{A_{LCP} + A_{RCP}} \cdot 200 \]
Chiral effects in hybrid metal-polystyrene metasurfaces

- Circular dichroism measurements: PAS difference between LCP and RCP

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

Chiral effects in hybrid metal-polystyrene metasurfaces

- Modelling with the metallic grid on the substrate

Chiral effects in hybrid metal-polystyrene metasurfaces

- Modelling with the metallic grid on the substrate: $\varphi=20^\circ$
Chiral effects in hybrid metal-polystyrene metasurfaces

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Chiral effects in hybrid metal-polystyrene metasurfaces

Experimental CD: $\theta$ dependence

- Ag
- Au
- Cr

$\theta = 25^\circ$, LCP

$\theta = 25^\circ$, RCP
Chiral effects in hybrid metal-polystyrene metasurfaces

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Going more planar

Polystyrene spheres (518nm diam)
Glass (1 mm)

Ion etching
Polystyrene spheres (around 480nm diam)
Glass (1 mm)

Metal flux (Au)
60°
Glass (1 mm)

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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

\[
Ext_{-45} = 1 - T_{-45} \\
Ext_{45} = 1 - T_{45} \\
CD[\%] = 100 \frac{Ext_{-45} - Ext_{45}}{Ext_{-45} + Ext_{45}}
\]
Sample AgC1
Going more planar

Sample AgC1

Sample AuA3

**A3: A_SLG-PS518_RIE929_EVA359 Au 52 nm tilt 45°+ in-plane 28°**
Going more *planar*

Sample AuA3

\[ ND = 1.0 \]

\[ \approx \text{chiral} \]
Going more planar

Sample AuD2

\[ ND = 1.0 \]

Sample AuD1

Experimental CD, Sample AuD2

Experimental CD, Sample AuD1
Going more planar

Experiment: in-plane rotation, normal incidence

\[ Ext_{-45} = 1 - T_{00,-45} \]
\[ Ext_{45} = 1 - T_{00,45} \]
\[ CD[\%] = 100 \frac{Ext_{-45} - Ext_{45}}{Ext_{-45} + Ext_{45}} \]

Experiment, Sample AuD1, CD

Experiment, Sample AuD2, CD
Going more planar

Simulations: elliptical nanoholes

\[ \theta = 0^\circ, RCP, LCP \]

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

Experiment, Sample AuD1, CD

Experiment, Sample AuD2, CD
Going more *planar*

Sample Au03

\[ |\theta| = 20^\circ \]
Going more *planar*

Sample Au03

Experiment, Sample Au03, T 0

Experiment, Sample Au03, T 0 long
Going more *planar*

Sample Au03

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Experiment, Sample Au03, T m45

Experiment, Sample Au03, T p45
Going more *planar*

Sample Au03
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.

Experimental CD: θ dependence

...to be continued
Literature


The End

That’s All Folks!!!!