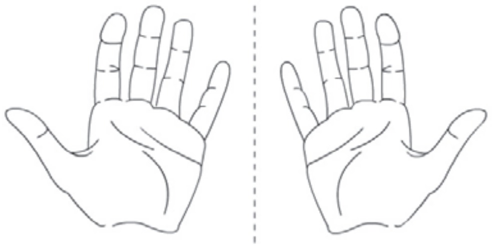
Helical assemblies of gold nanorods and silver nanowires into chiral thin films with giant circular dichroism

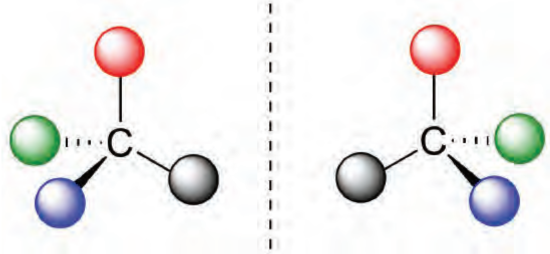
Sribharani Sekar, Wenbing Wu, Vincent Lemaire

Matthias Pauly

Institut Charles Sadron (Université de Strasbourg/CNRS)

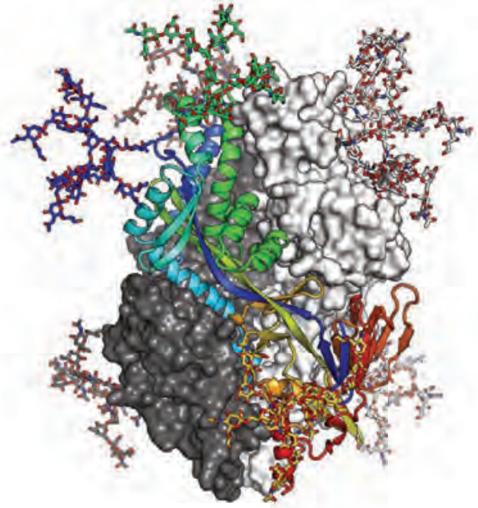
Chirality





Chiral objects
(molecules, nanostructures, macroscopic scale…)
$\longrightarrow$ ***lack mirror symmetry***

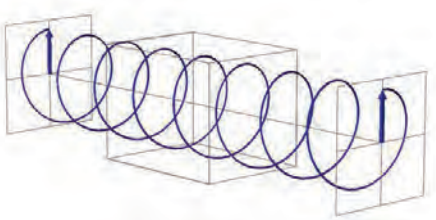
Battles et al. *Nat Commun* 2017 8, 1528



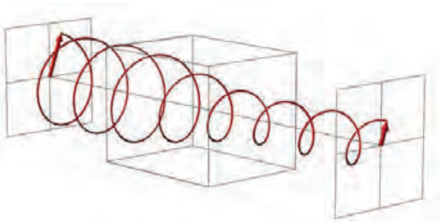
Circular Dichroism

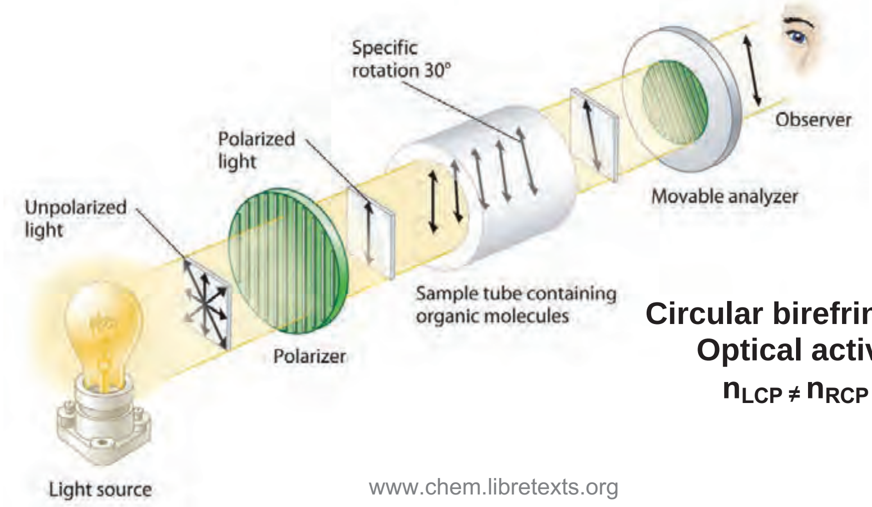
$\Delta A = A_{LCP} - A_{RCP}$

Right-handed circularly polarized light (RCP)



Left-handed circularly polarized light (LCP)





www.chem.libretexts.org

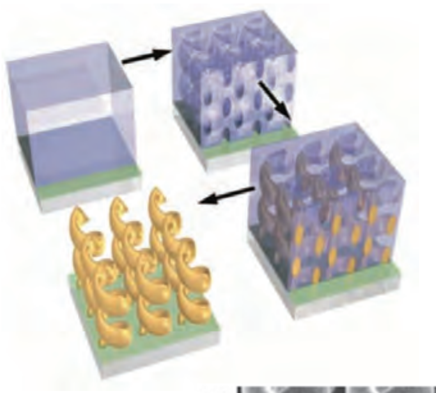
Circular birefringence
Optical activity
$n_{LCP} \neq n_{RCP}$

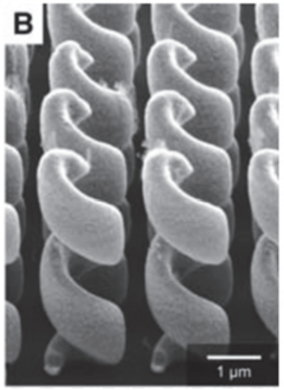
Chiral plasmonic nanoparticles

Top-down fabrication

Bottom-up approaches

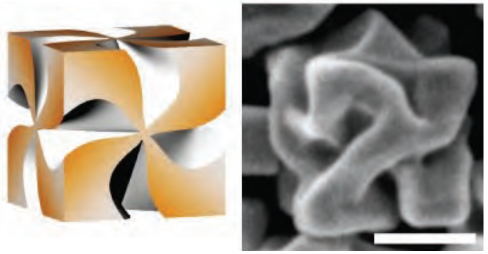
Review: W. Wu and M. Pauly, *Mater. Adv.* 2022, 3, 186-215.

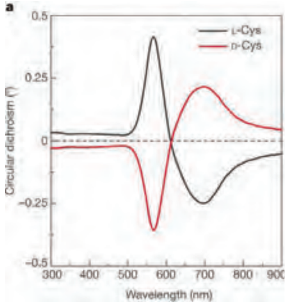


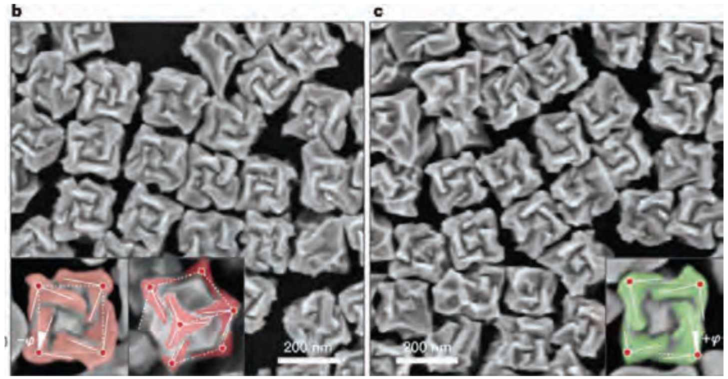


gold helices obtained by laser direct writing

Gansel et al. *Science* 2009, 325, 1513-1515.

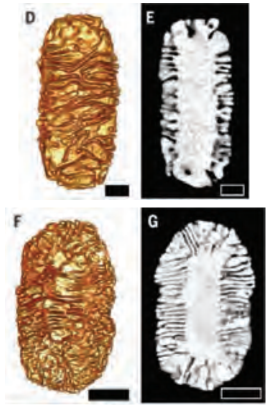


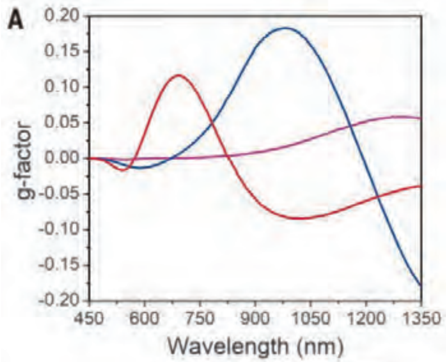


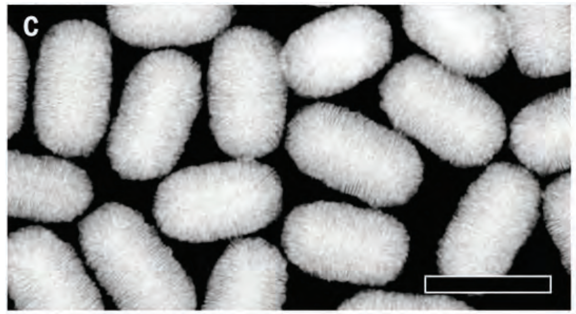


432 helicoid III, grown on a gold octahedral seed in presence of chiral aminoacids

H.-E. Lee et al. *Nature*, 2018, 556, 360–365.





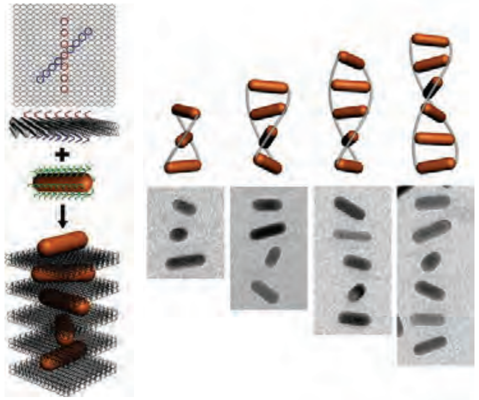


chiral gold nanorods, grown in presence of chiral surfactants

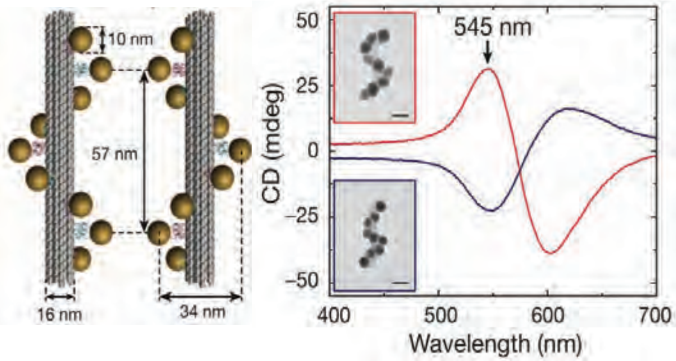
G. González-Rubio et al. *Science*, 2020, 368, 1472.

Plasmonic chiral metamaterials: chiral assembly of non-chiral nanoparticles

Review: W. Wu and M. Pauly, *Mater. Adv.* 2022, 3, 186-215.

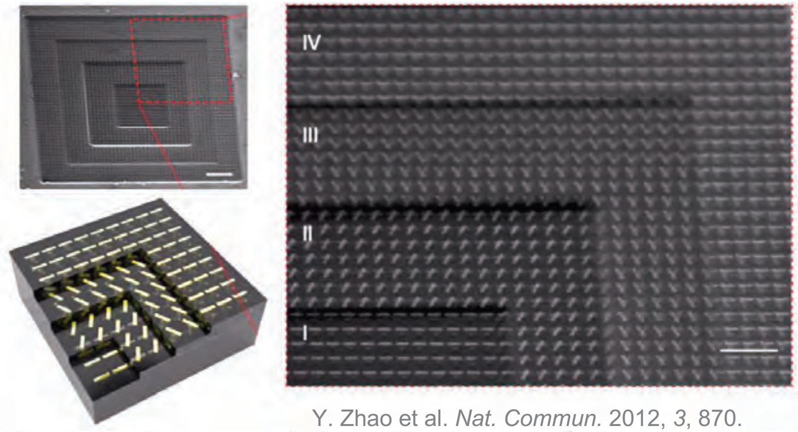


Lan et al. *J. Am. Chem. Soc.* 2015, 137, 1, 457–462

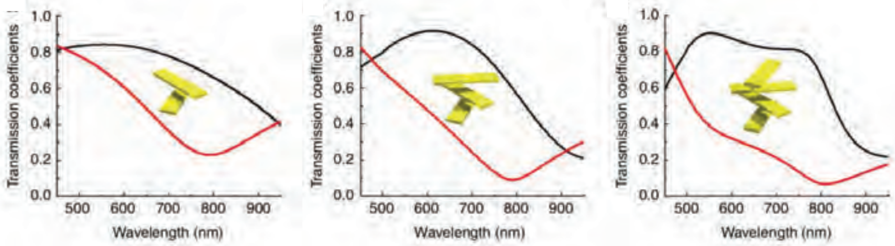


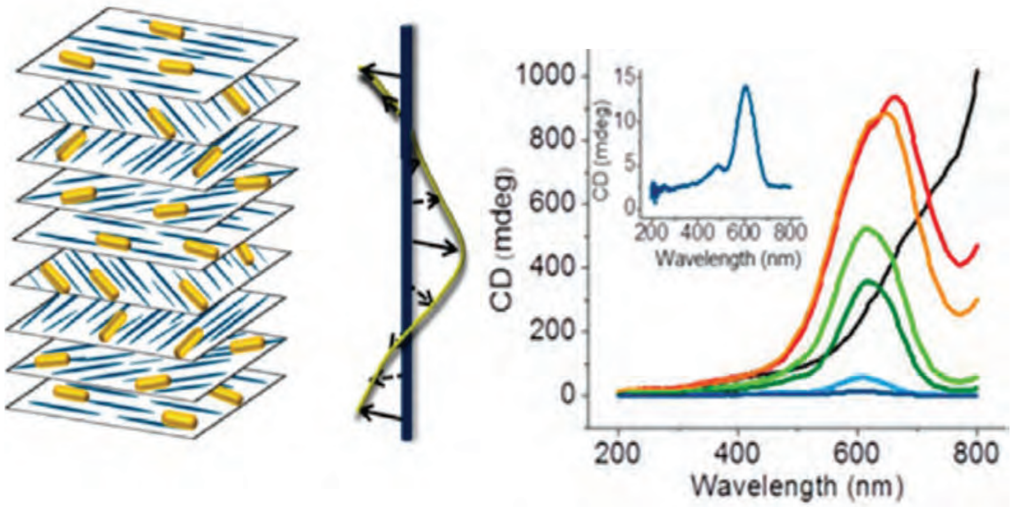
Kuzyk et al. *Nature* 2012, 483, 311-314.

Cheng et al. *ACS Nano* 2017, 11, 4, 3806–3818



Y. Zhao et al. *Nat. Commun.* 2012, *3*, 870.

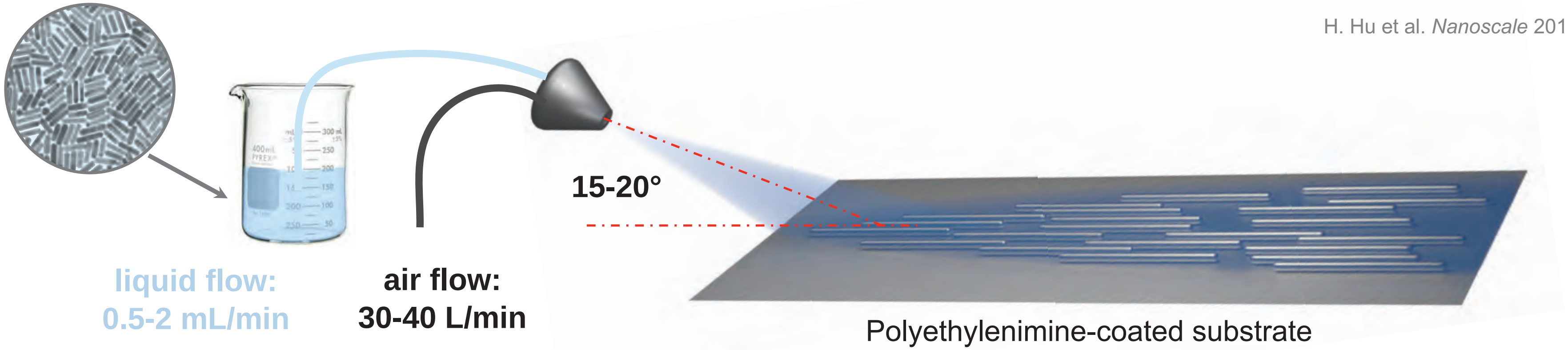




Querejeta-Fernández et al. *J. Am. Chem. Soc.* 2014, 136, 4788-4793.

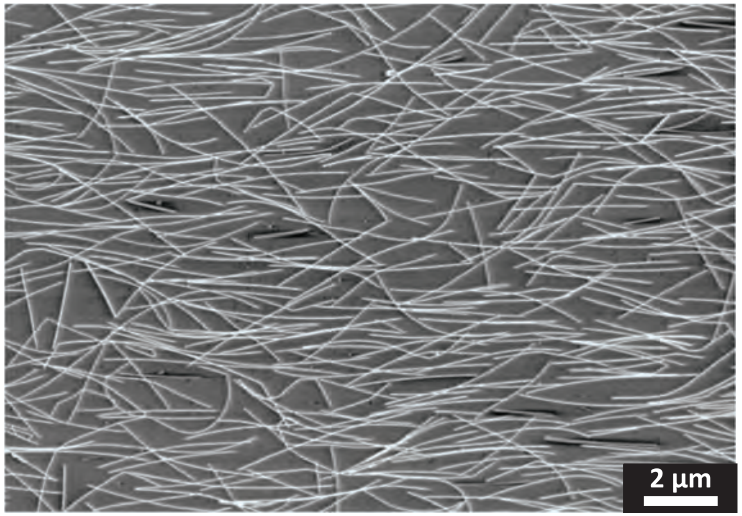
Grazing Incidence Spraying (GIS)

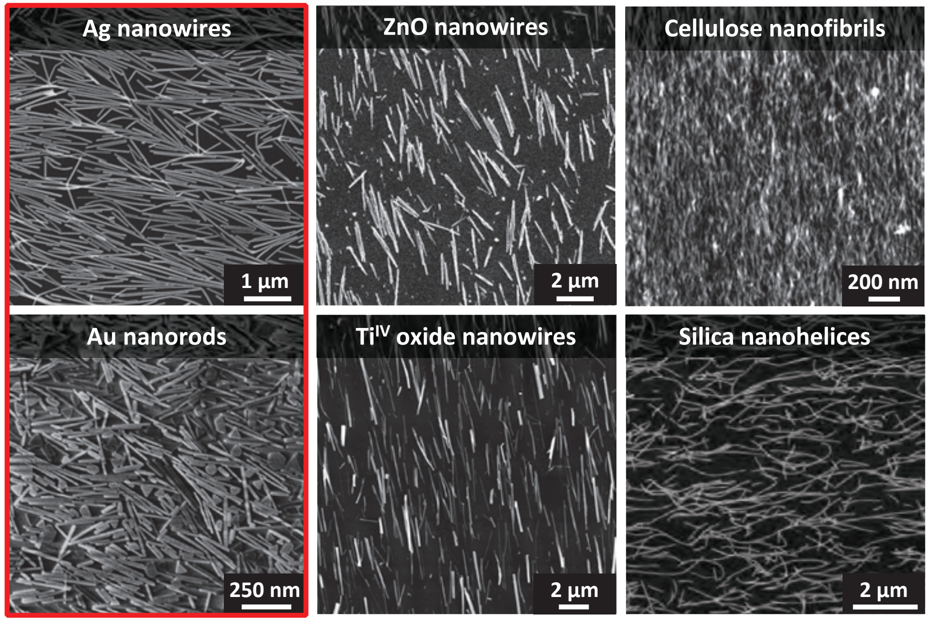
H. Hu et al. *Nanoscale* 2017, 9 (3), 1307-1314.



Ag nanowires@PVP

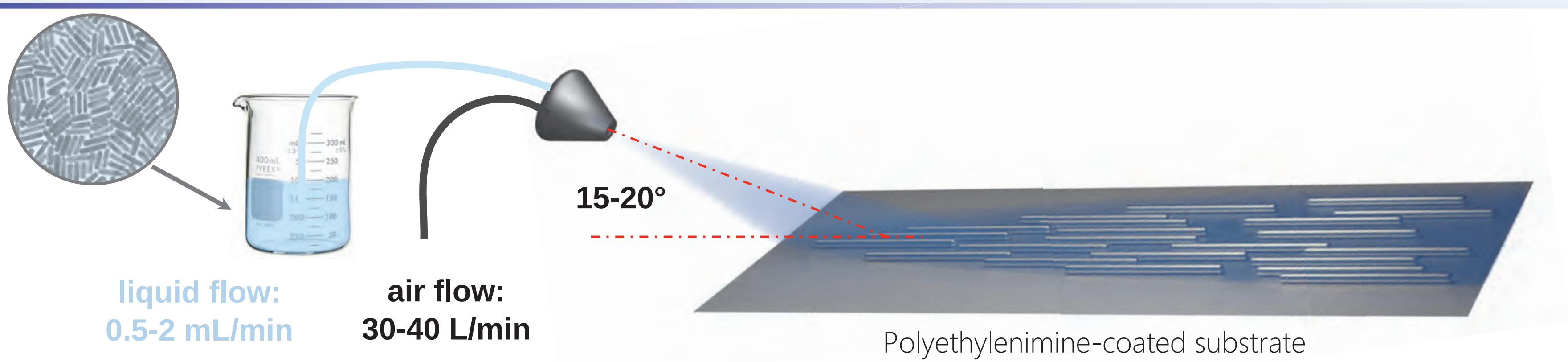
d ≈ 60 nm, L ≈ 6 μm





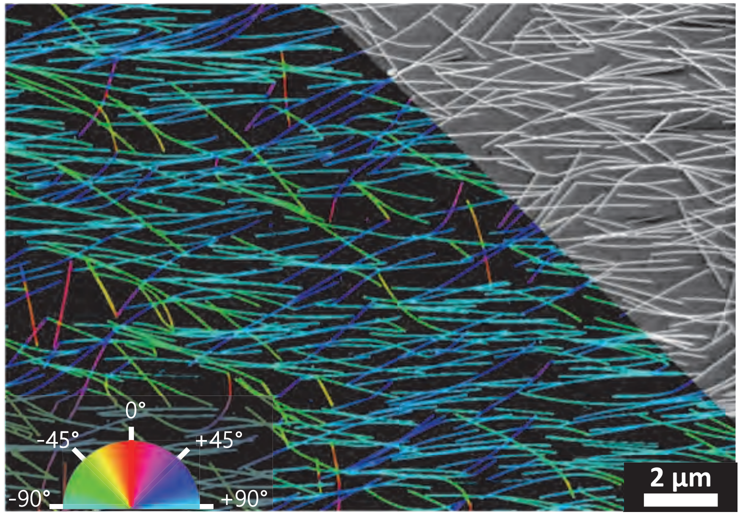
S. Sekar et al. *Faraday Discuss.* 2016, 191, 373-389.
Blell et al. *ACS Nano* 2017, *11*, 84-94.
Gao et al. *ACS Nano* 2020, *14*, 4111-4121.
M. Taner et al. *Nanoscale* 2021, *13*, 8958-8965.

Grazing Incidence Spraying (GIS)



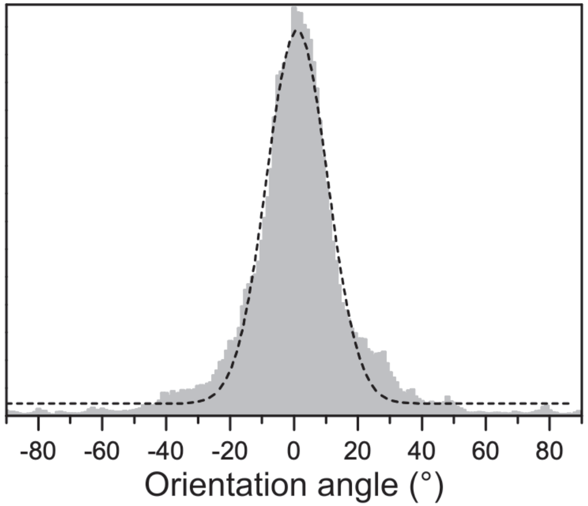
Ag nanowires@PVP

$d \approx 60$ nm, $L \approx 6$ µm



Orientation analysis made with OrientationJ for ImageJ

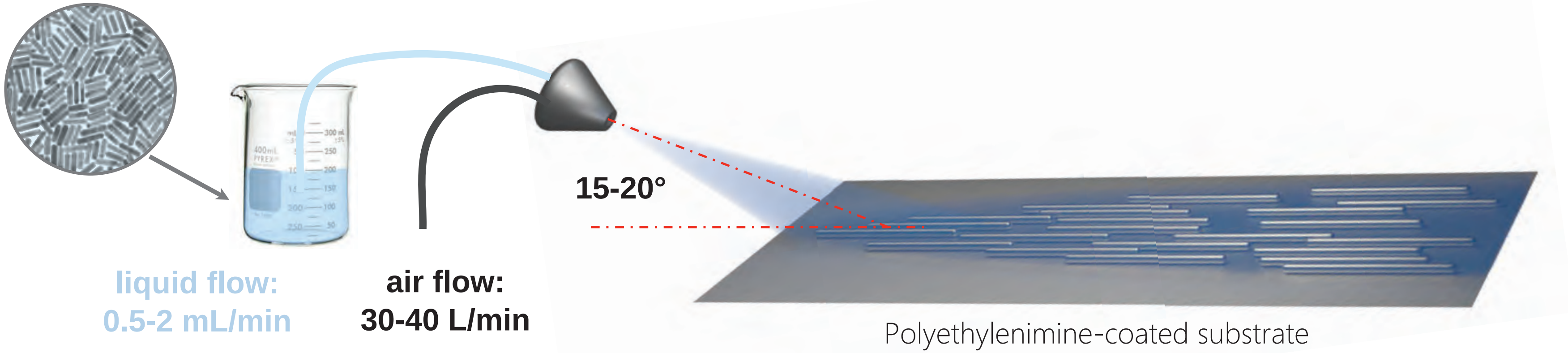
H. Hu et al. Nanoscale 2017, 9 (3), 1307-1314.



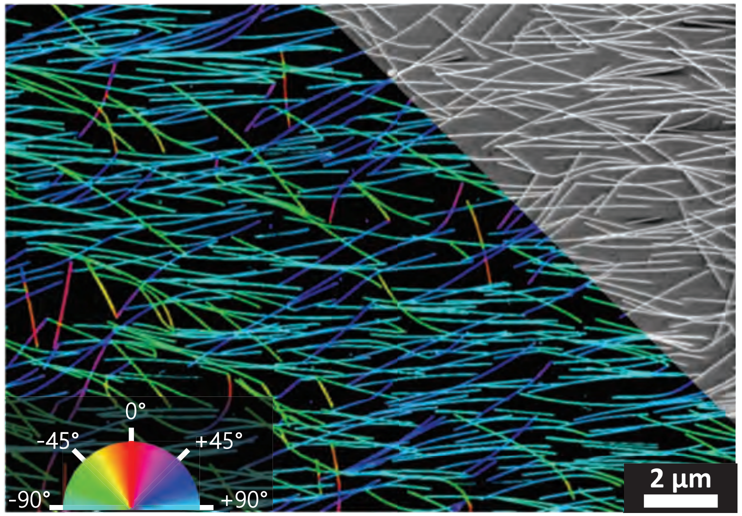
$$S_{2D} = \langle 2cos^2\theta - 1 \rangle = 0.88$$

85% of AgNWs within ± 20°

Grazing Incidence Spraying (GIS)



Ag nanowires@PVP
d ≈ 60 nm, L ≈ 6 µm



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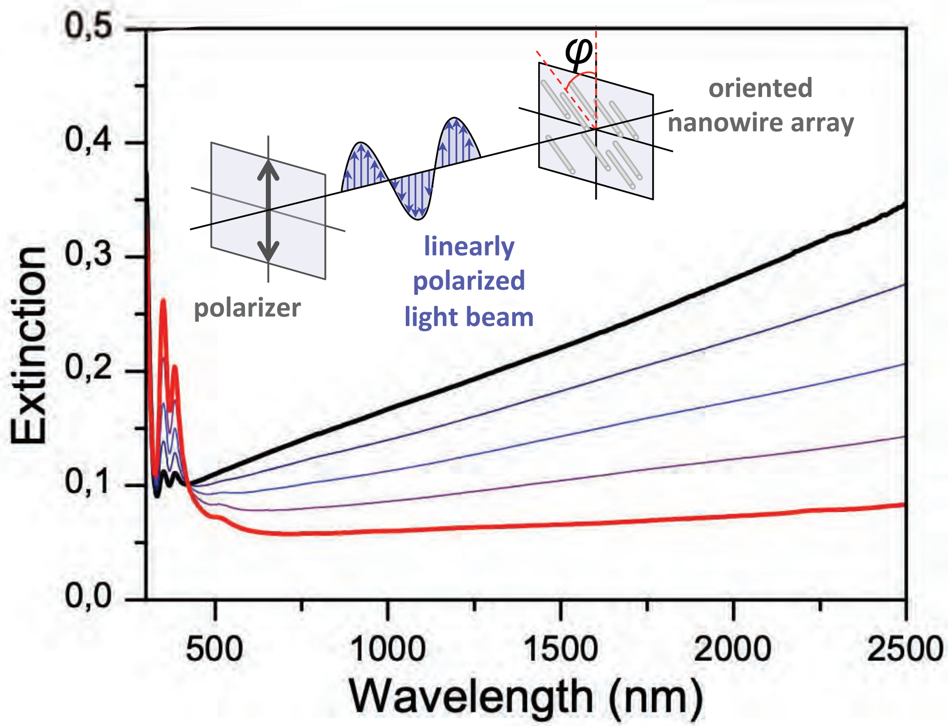
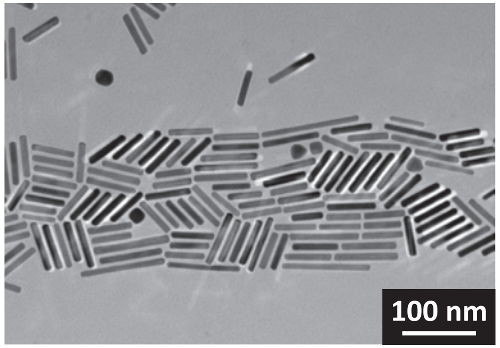
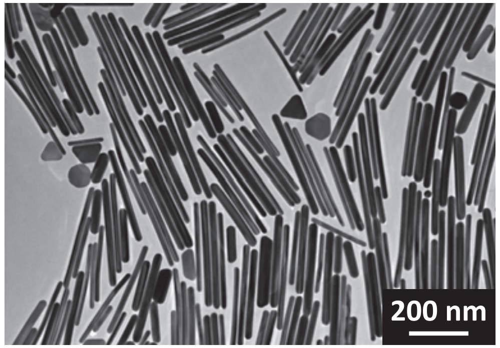


GIS orientation: effect of nanorod/nanowire length



S-AuNRs

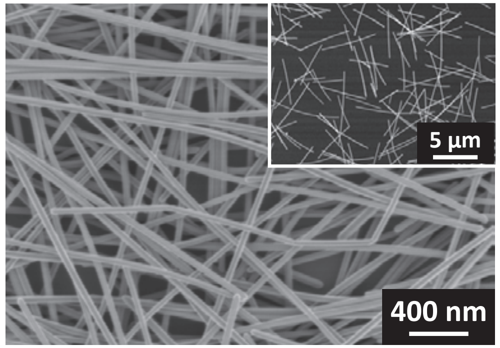
L = 128 ± 16 nm
d = 17 ± 2 nm
AR = 7



L-AuNRs

L = 245 ± 50 nm
d = 15 ± 3 nm
AR = 16

post-functionalized with PVP



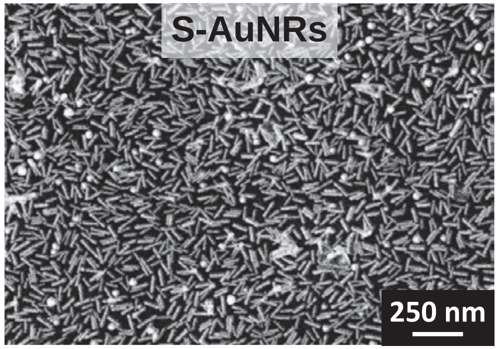
AgNWs

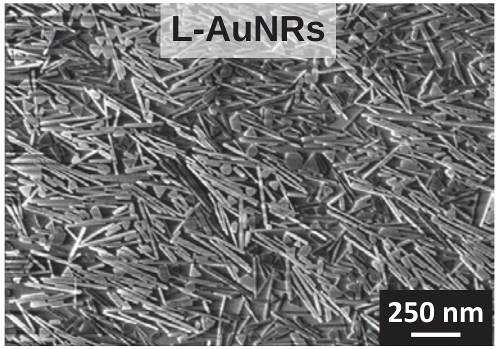
L = 5.7 ± 1.7 µm
d = 51 ± 6 nm
AR = 110

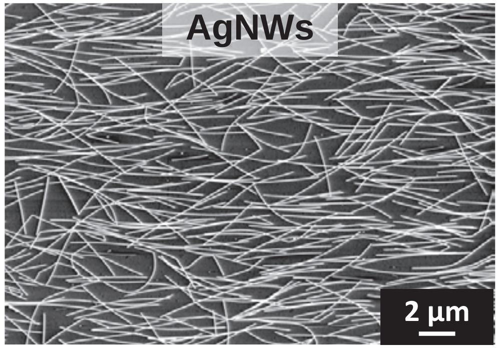
coated in-situ by PVP

S. Sekar et al. *Faraday Discuss.* **2016**, *191*, 373-389.

GIS orientation: effect of nanorod/nanowire length







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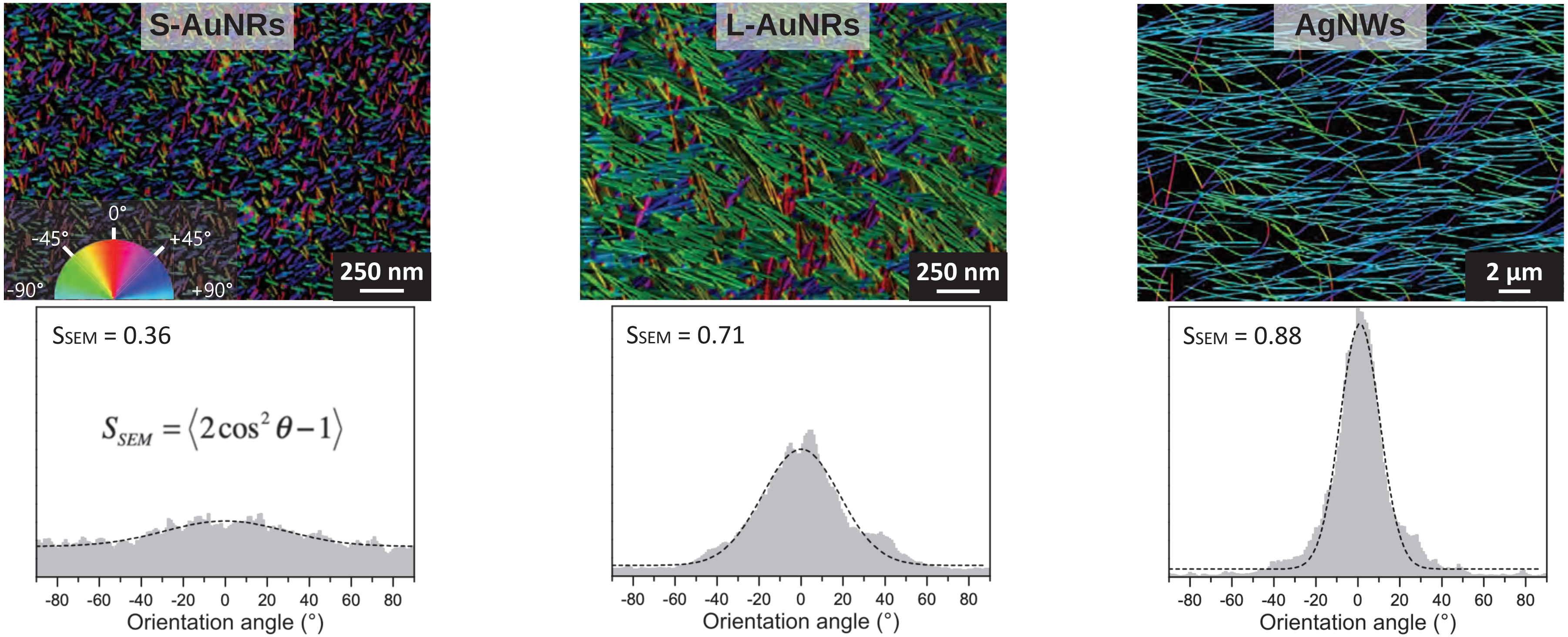
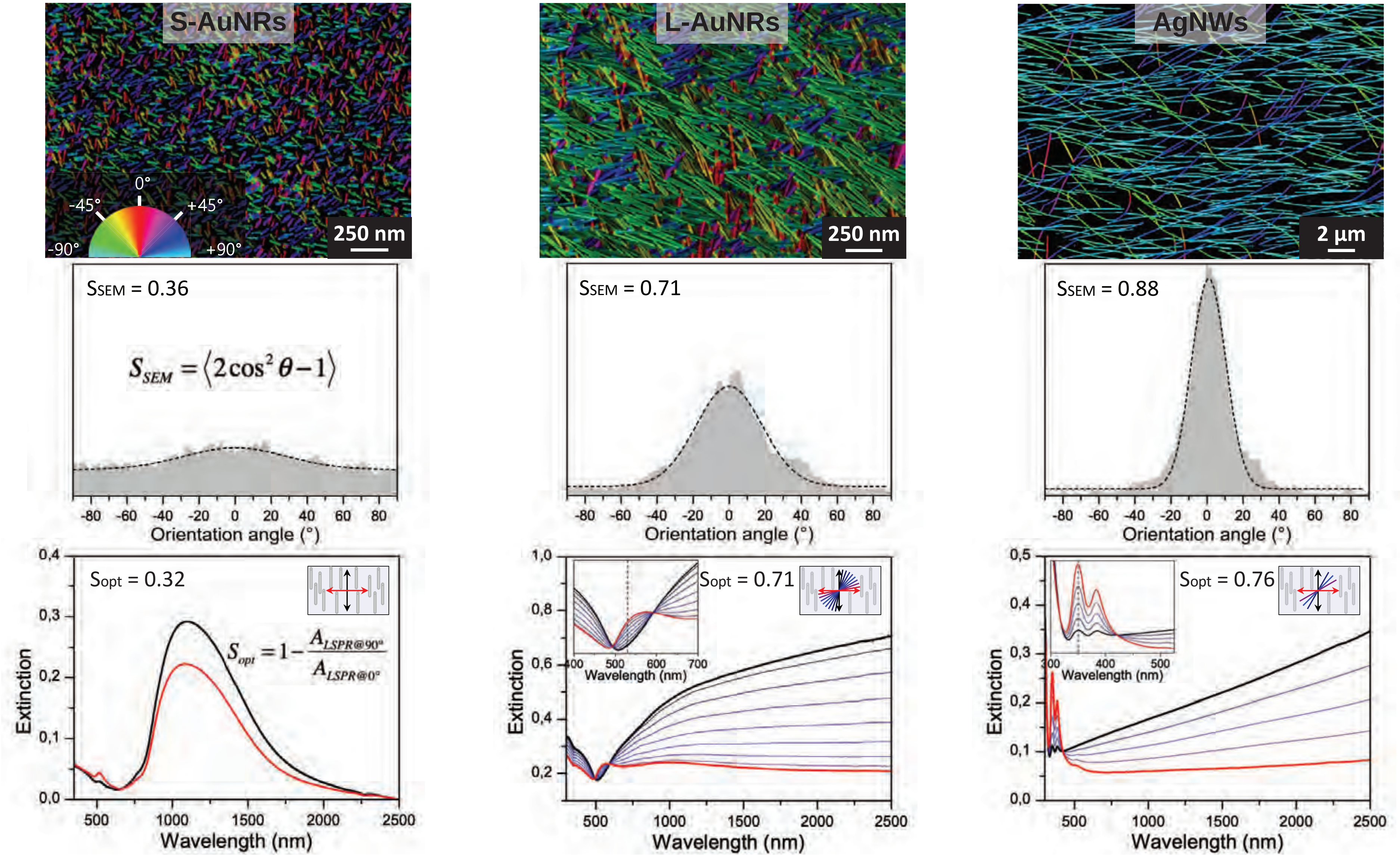
GIS orientation: effect of nanorod/nanowire length

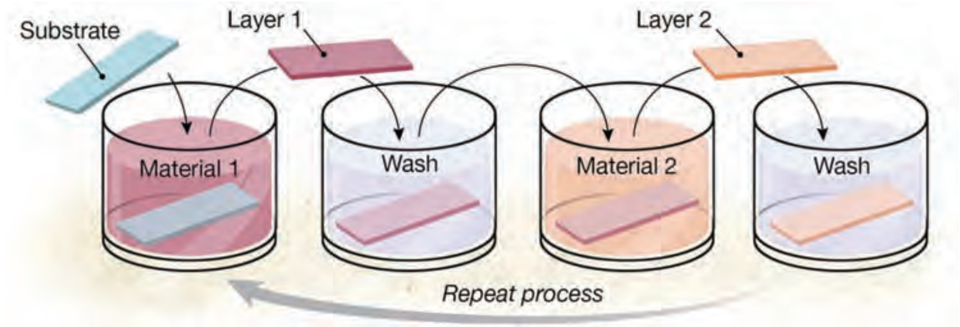


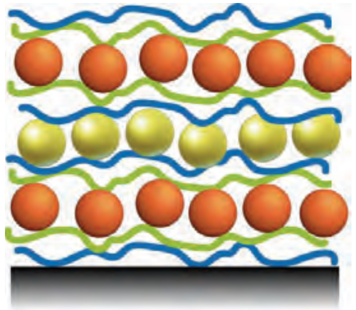
S. Sekar et al. *Faraday Discuss.* **2016**, *191*, 373-389.

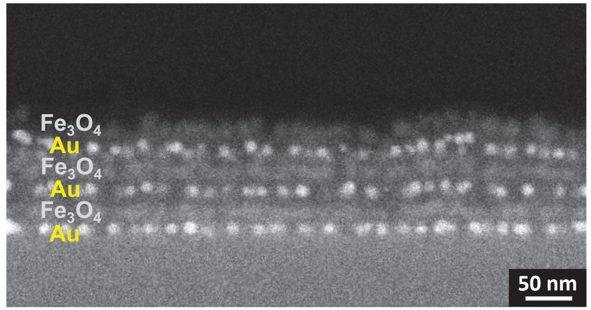
GIS orientation: effect of nanorod/nanowire length



Towards complex and tunable superstructures

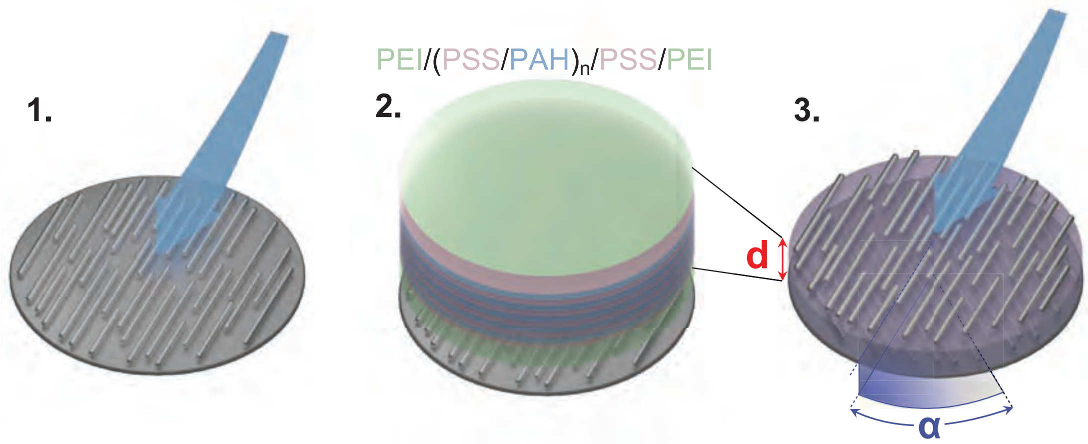


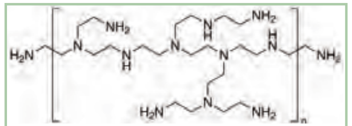




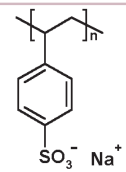
alternating layers of polyelectrolytes, Au and Fe_3O_4 NPs

G. Decher, *Science* 1997, 277 *(5330)*, 1232-1237
J. J. Richardson et al. *Science* 2015, 348, aaa2491.

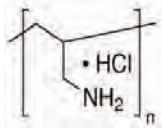




Poly(ethylene imine) (PEI)



Poly(sodium styrene sulfonate) (PSS)

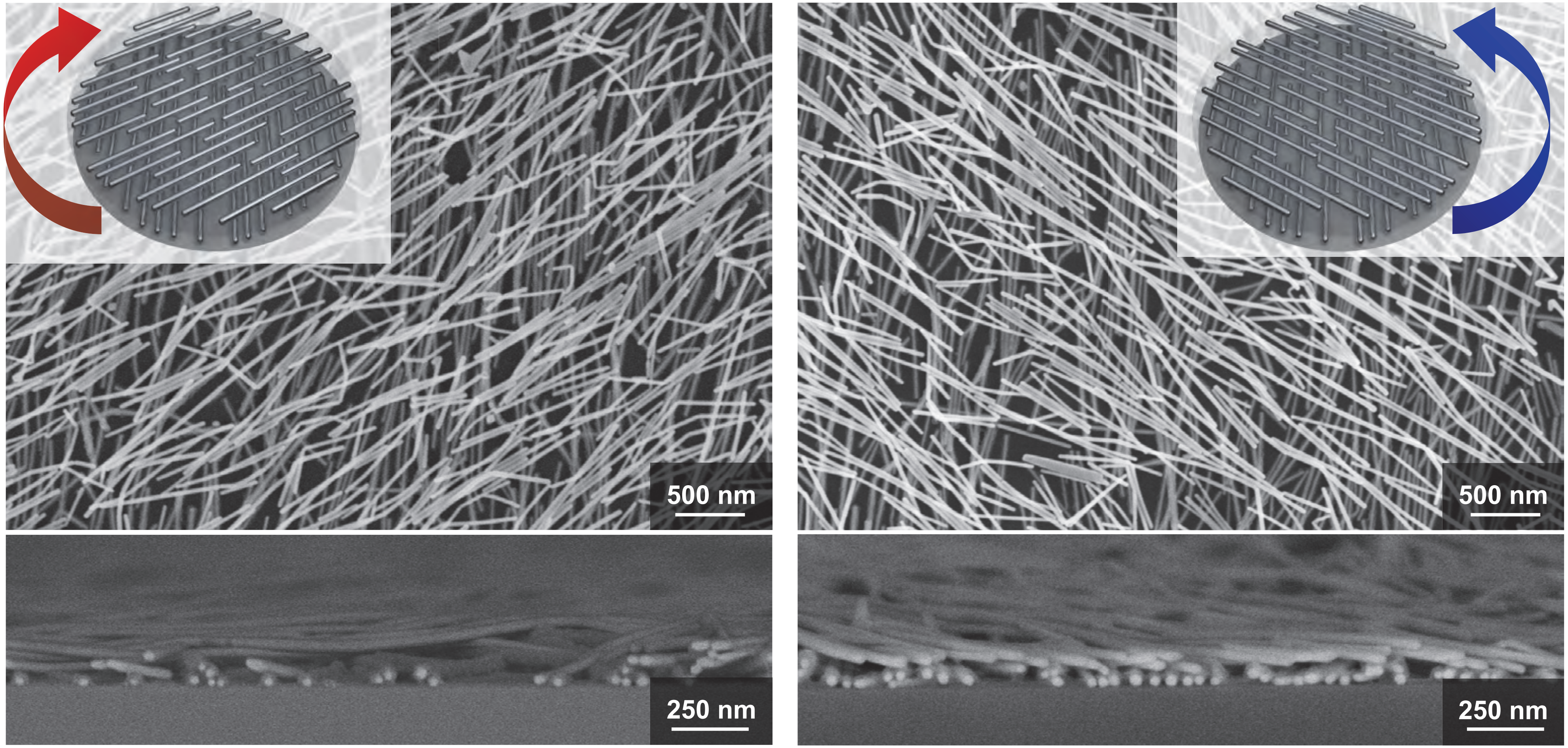


Poly(allylamine hydrochloride) (PAH)

→ **perfect control on the sequence of materials (polymers, nanoparticles, molecules, etc…)**

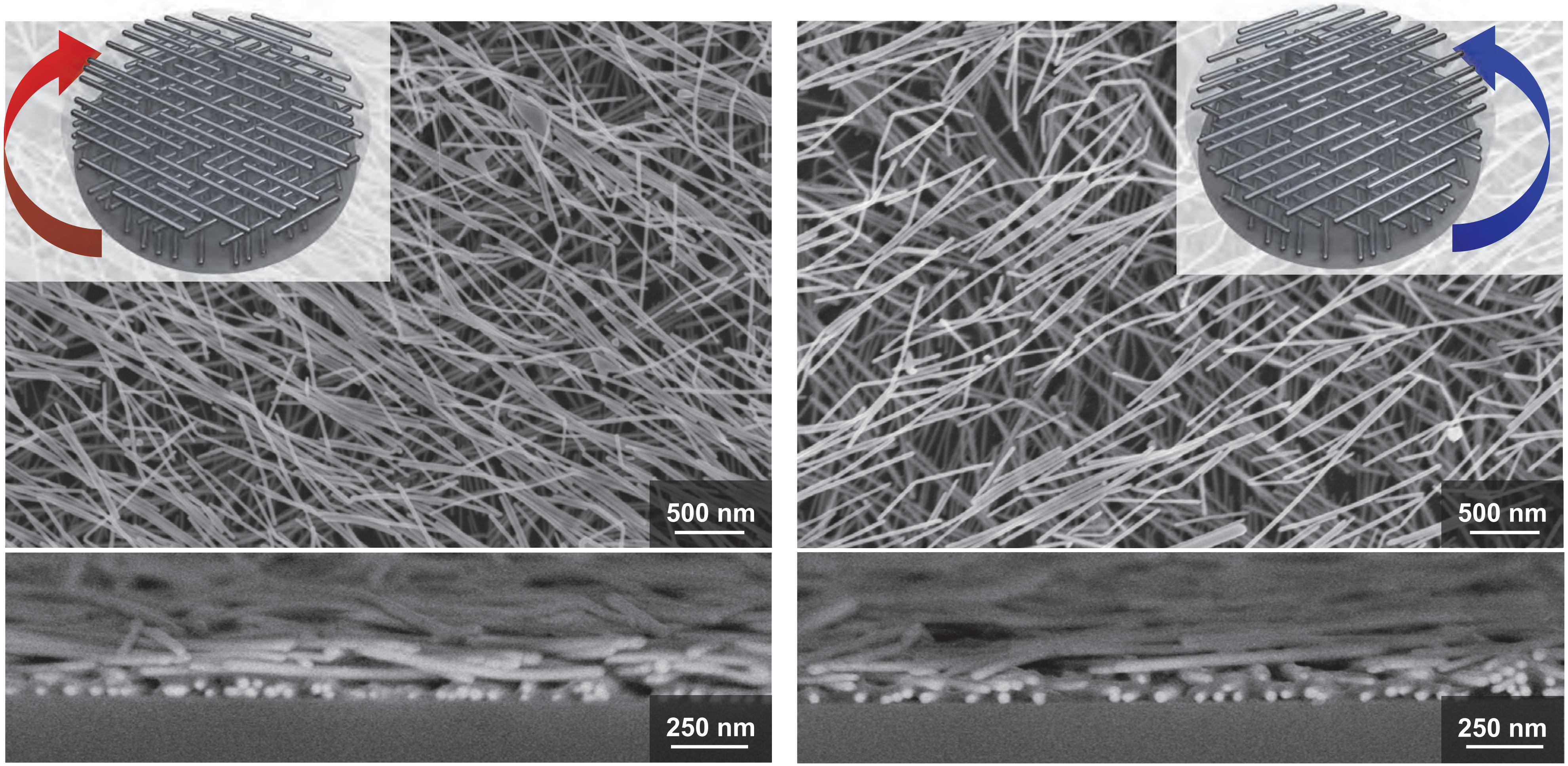
→ **nm-scale control of the distance between nanoparticle layers**

Helical assemblies: AgNWs



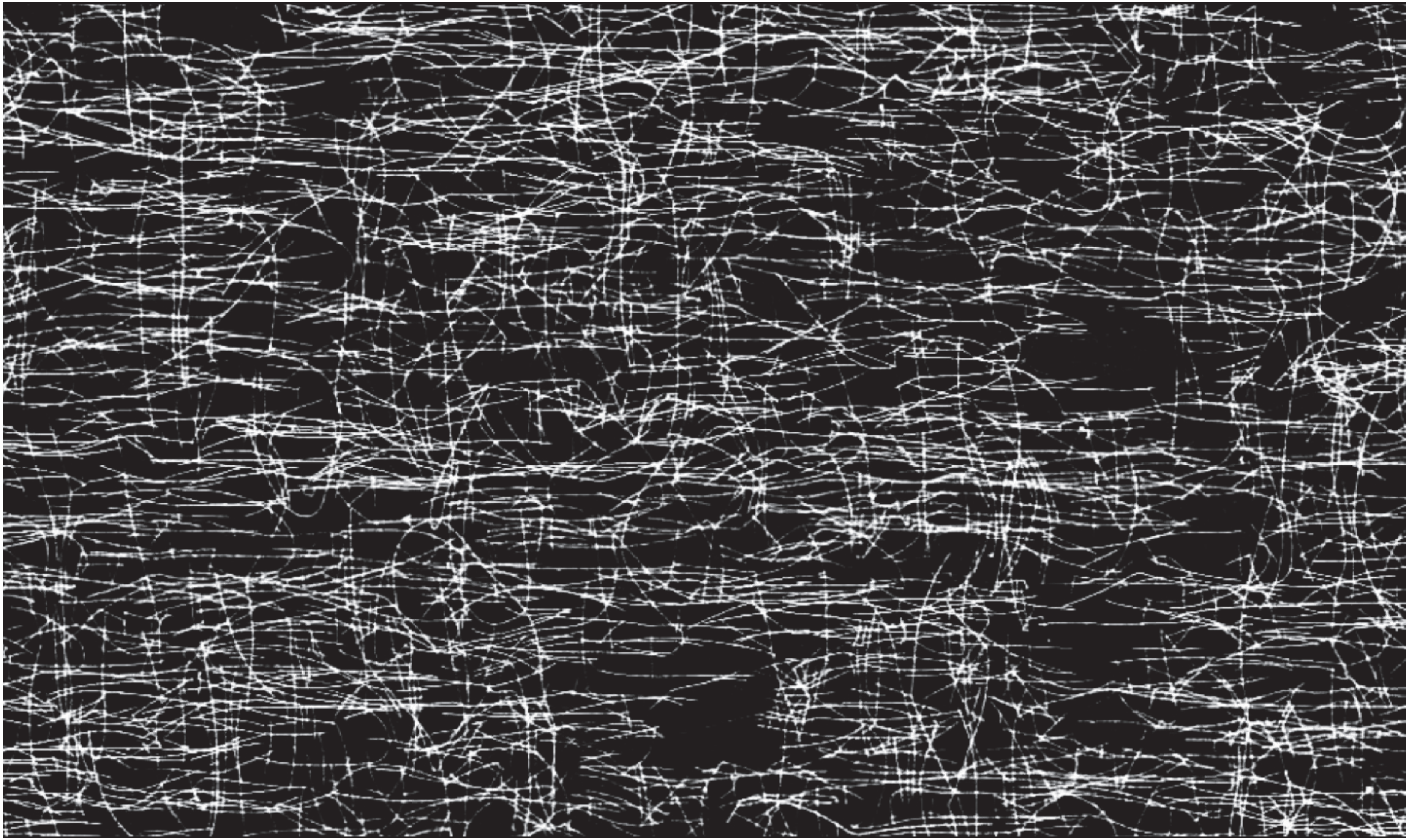
H. Hu et al. *ACS Nano* 2021, *15*, 13653-13661.

Helical assemblies: AgNWs



H. Hu et al. *ACS Nano* 2021, *15*, 13653-13661.

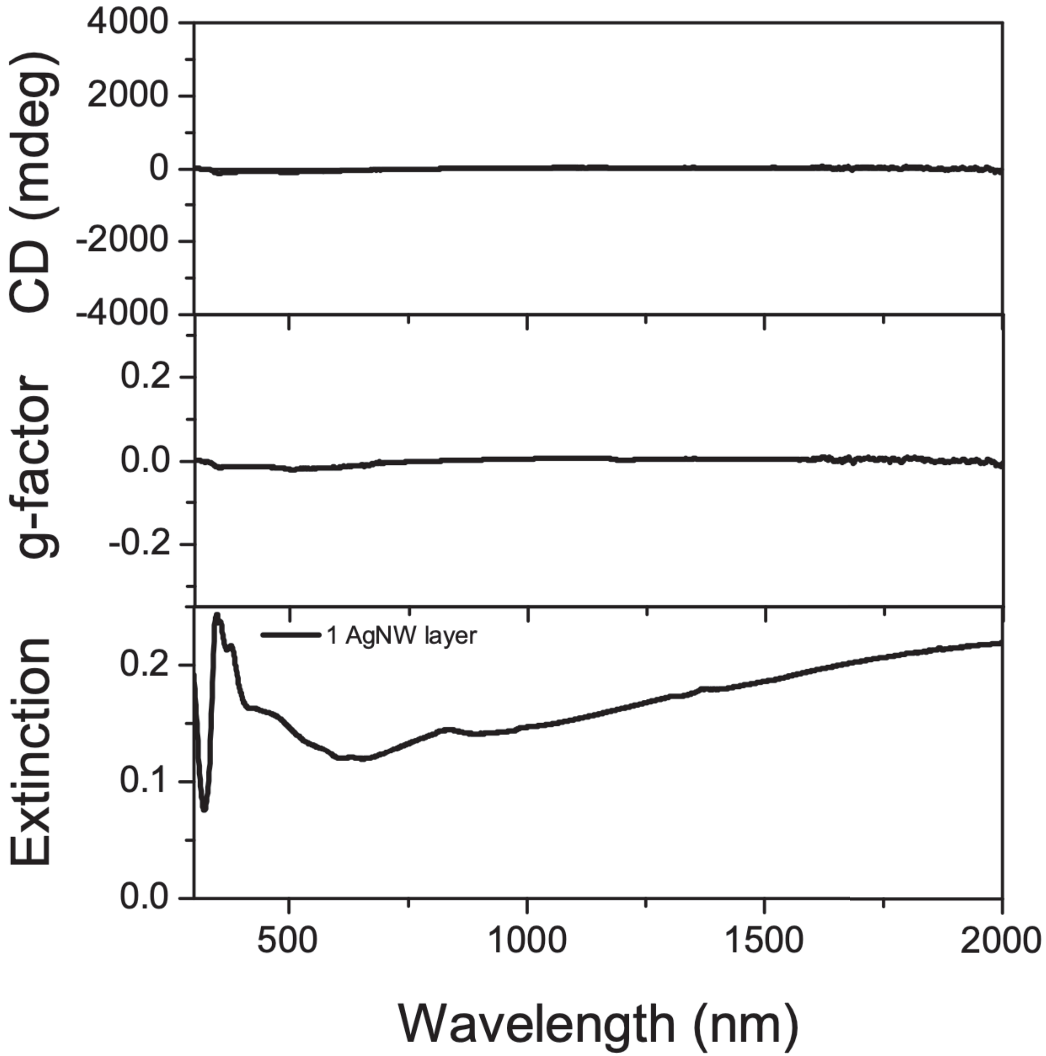
Macroscopic-scale assembly of oriented AgNWs



Building chiral assemblies: AgNWs

Circular dichroism
CD
$\Delta A = A_{LCP} - A_{RCP}$

g-factor
$\Delta A/A$



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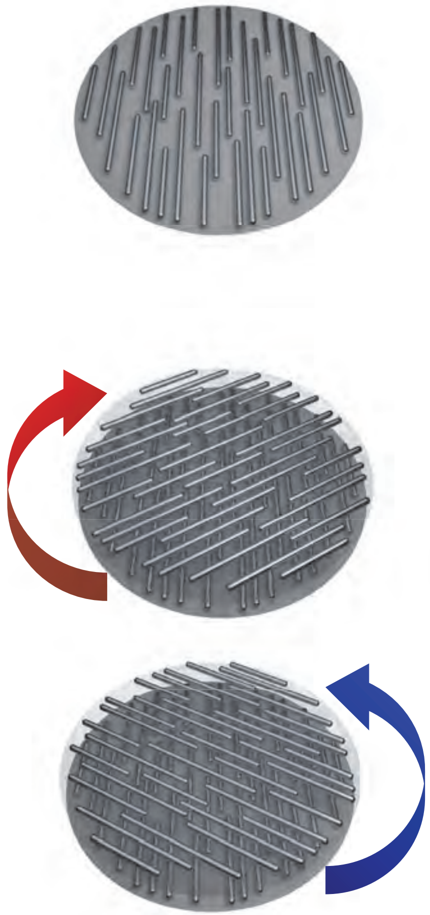
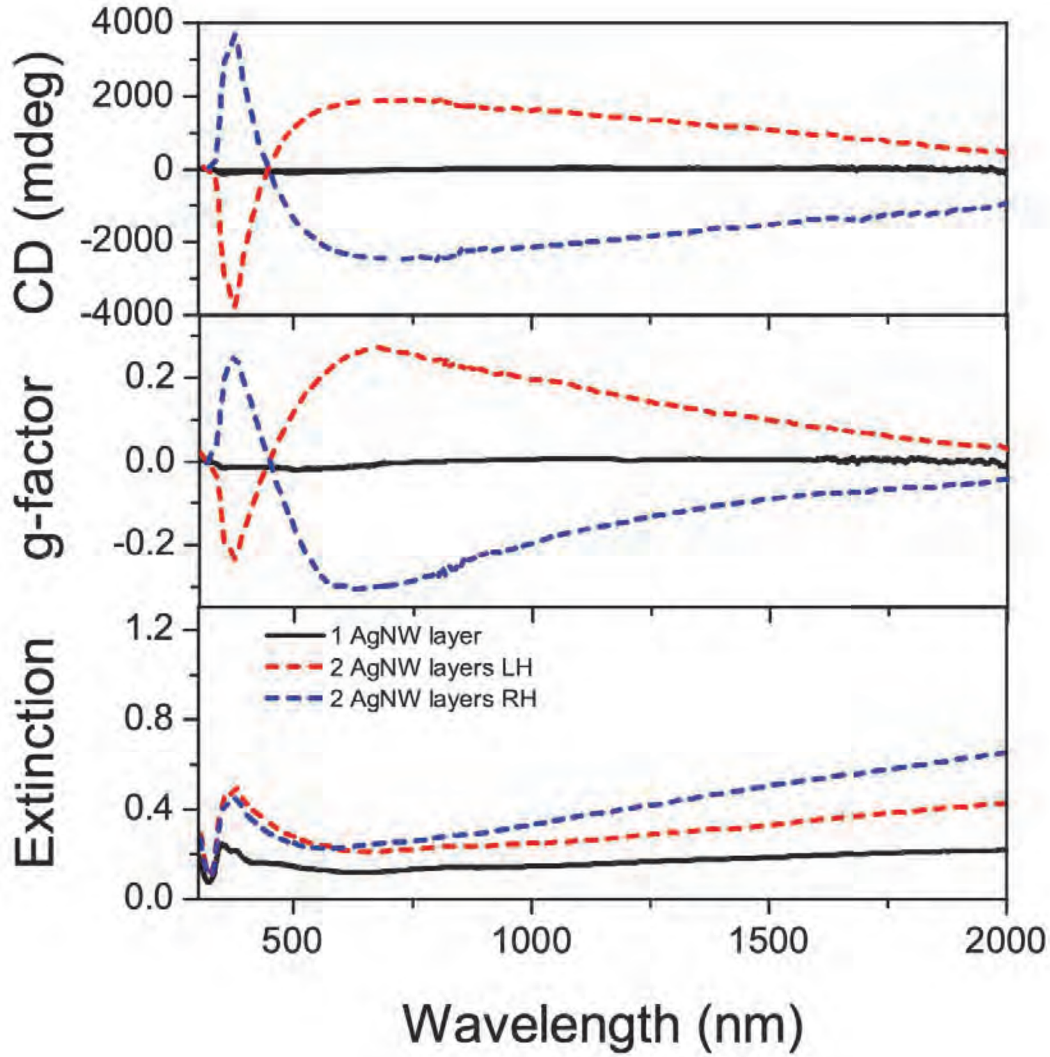
Building chiral assemblies: AgNWs



Circular dichroism
CD
$\Delta A = A_{LCP} - A_{RCP}$

g-factor
$\Delta A/A$



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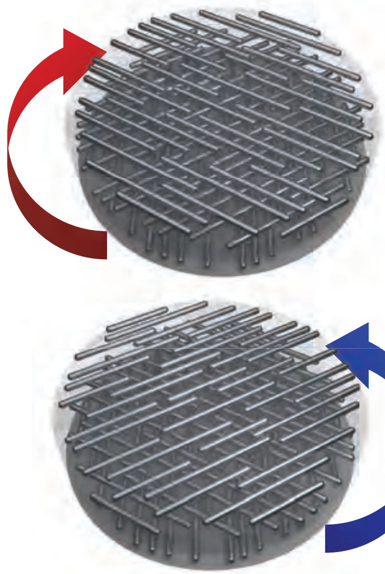
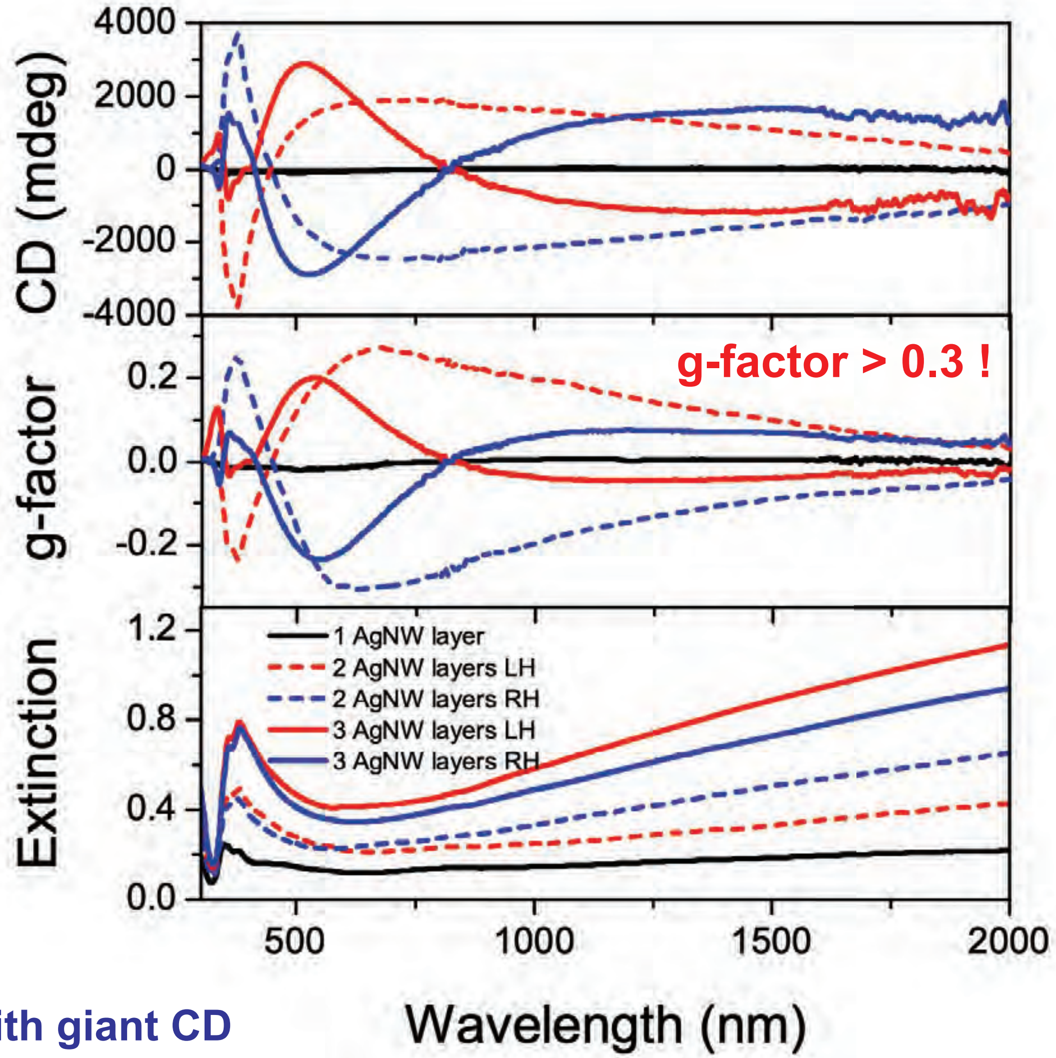
Building chiral assemblies: AgNWs

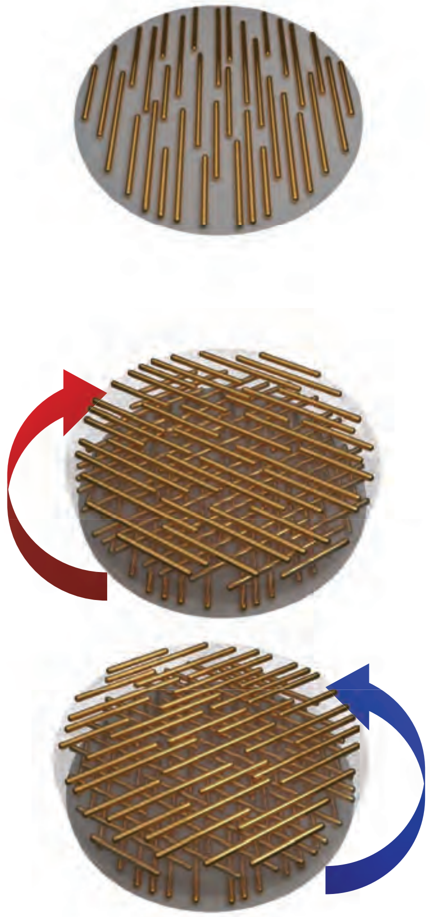


Circular dichroism
CD
$\Delta A = A_{LCP} - A_{RCP}$

g-factor
$\Delta A/A$

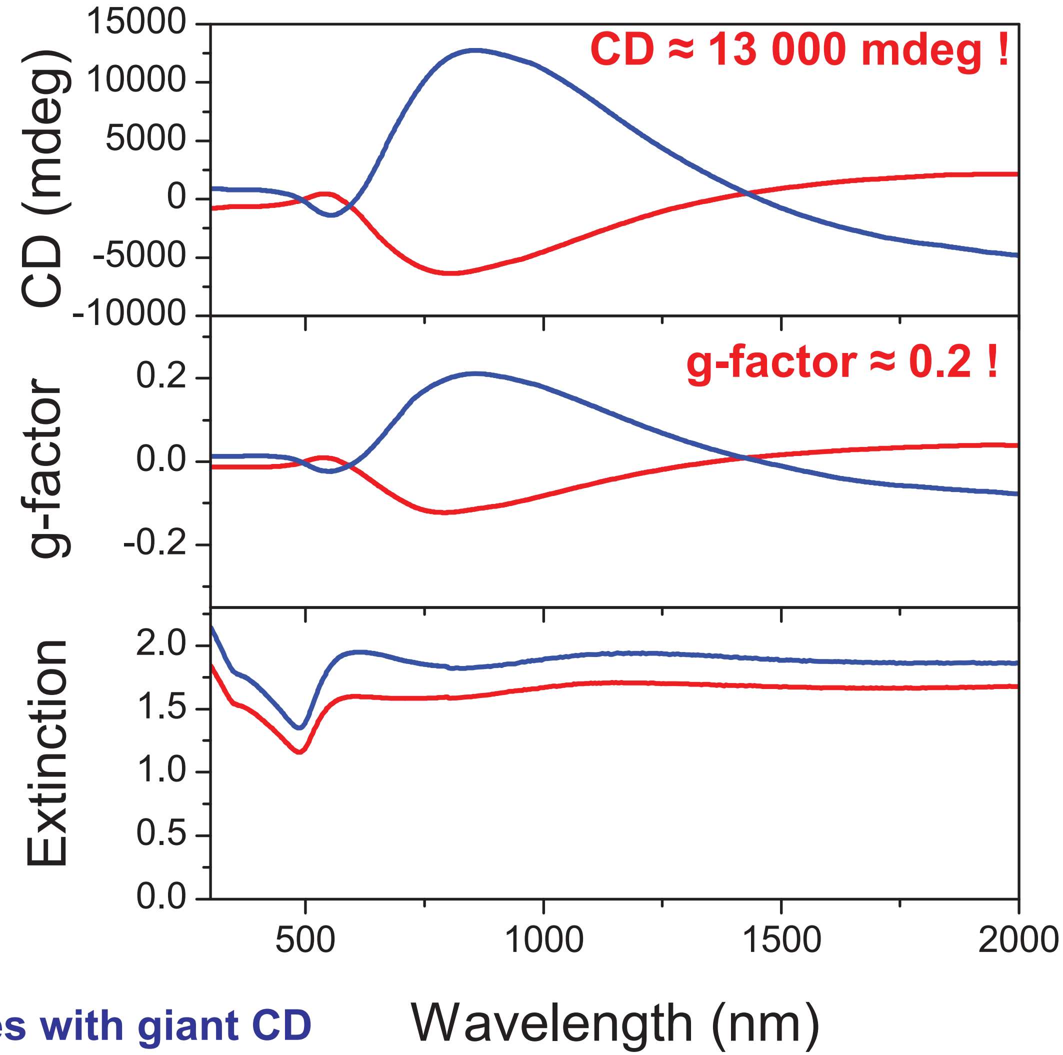


Structure-dependent chiral assemblies with giant CD



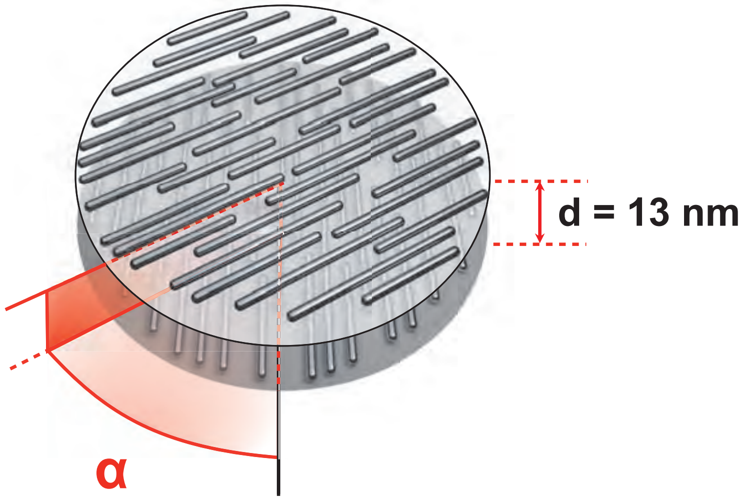
Circular dichroism
CD
$\Delta A = A_{LCP} - A_{RCP}$

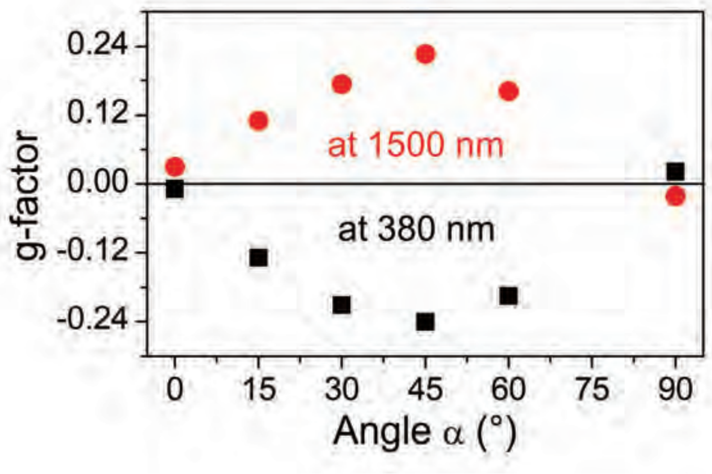
g-factor
$\Delta A/A$

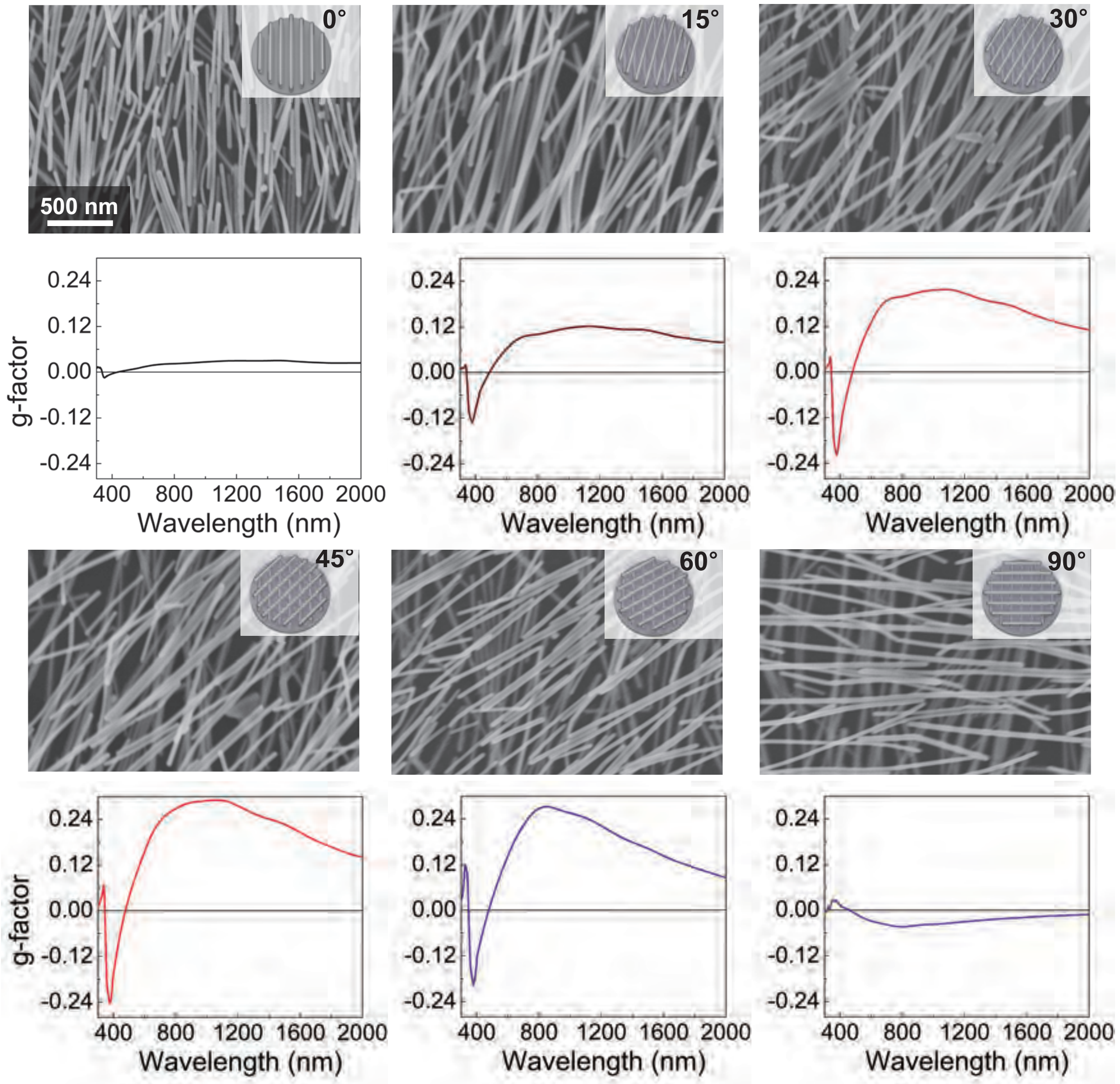


→ Composition-dependent chiral assemblies with giant CD

Angle-dependent CD: AgNWs



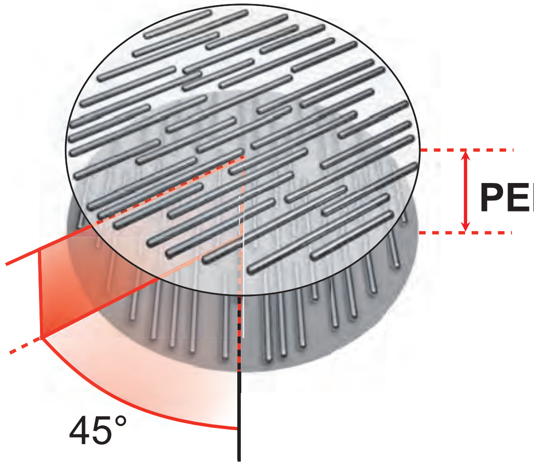


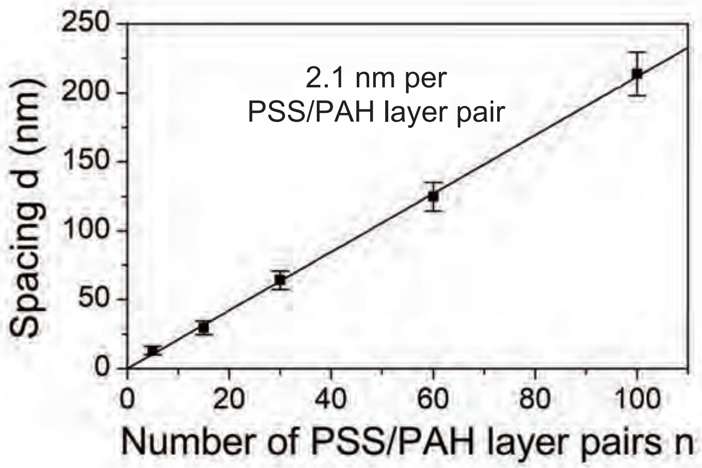


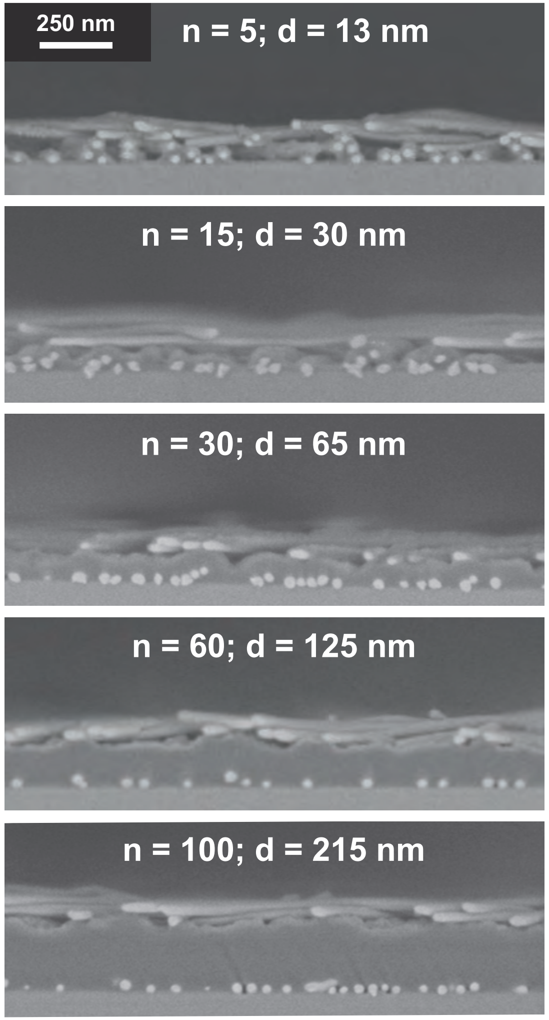
→ **CD intensity tuned by angle α**

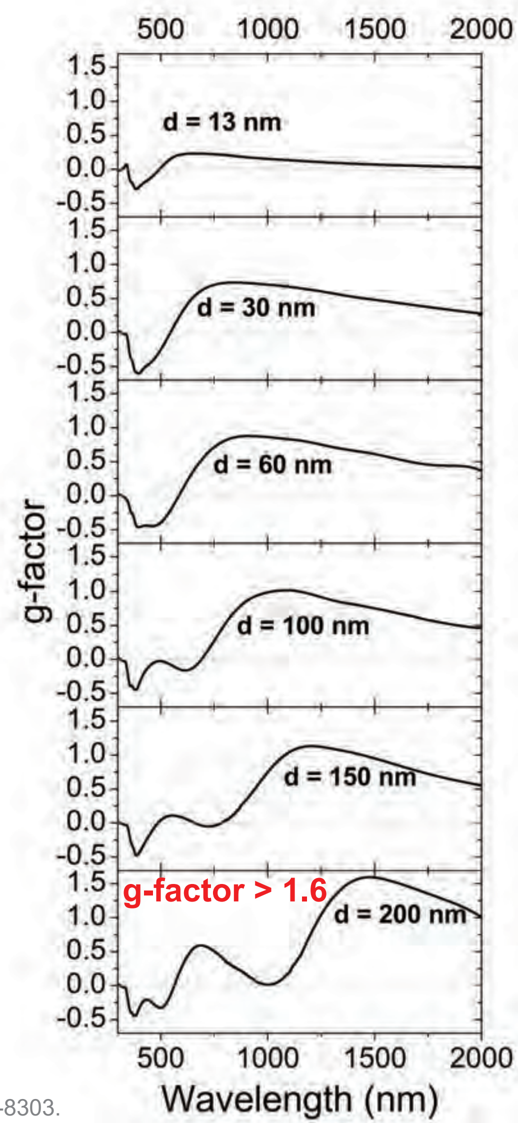
W. Wu et al. *Nano Lett.* 2021, *21*, 8298-8303.

Spacing-dependent CD: AgNWs









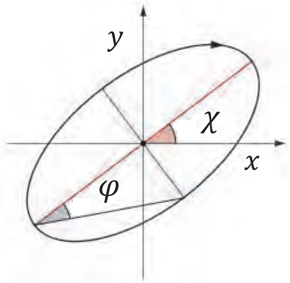
➡ **nm-scale control on the interlayer spacing**

W. Wu et al. *Nano Lett.* 2021, *21*, 8298-8303.

Coll. Yann Battie, Univ. de Lorraine
Oriol Arteaga, Univ. Barcelona

Light polarization state described by the Stokes Vector

$$S = \begin{bmatrix} I \\ I_x - I_y \\ I_{45^\circ} - I_{-45^\circ} \\ I_+ - I_- \end{bmatrix} = \begin{bmatrix} I \\ Ipcos(2\varphi)cos(2\chi) \\ Ipcos(2\varphi)sin(2\chi) \\ Ipsin(2\varphi) \end{bmatrix}$$

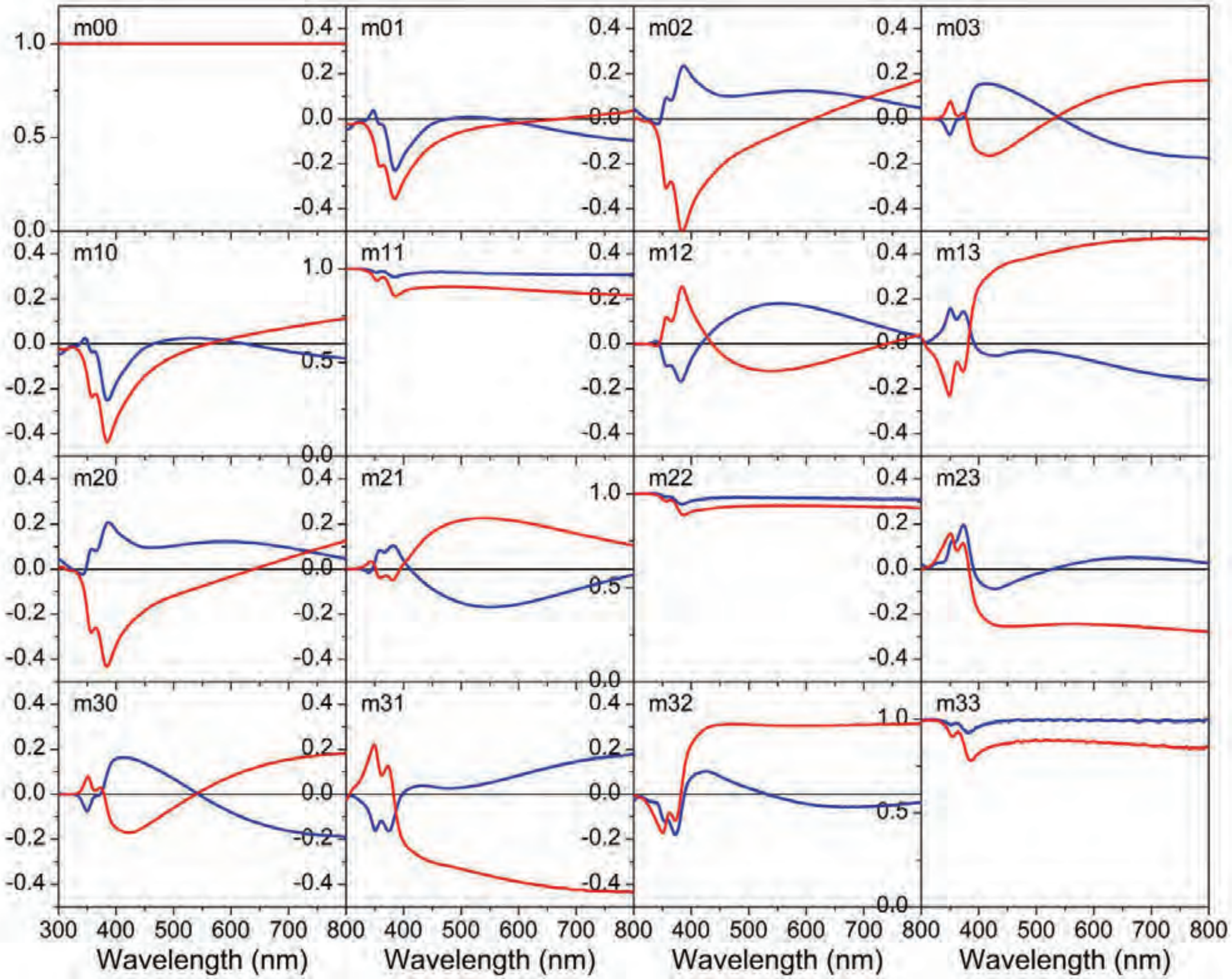


I Intentsity
p Degree of polarization
χ Azimuth
φ Ellipticity

Mueller Matrix describes the sample effect on S_{in}

$$S_{out} = M\ S_{in} \qquad M = \begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix}$$

$$M = \exp\begin{pmatrix} A & -LD & -LD' & CD \\ -LD & A & CB & LB' \\ -LD' & -CB & A & -LB \\ CD & -LB' & LB & A \end{pmatrix}$$



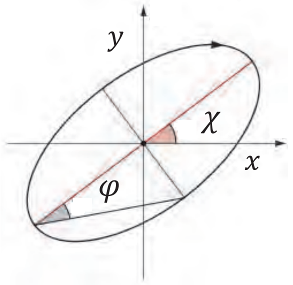
H. Hu et al. *ACS Nano* 2021, *15*, 13653-13661.

Mueller Matrix Polarimetry

Coll. Yann Battie, Univ. de Lorraine
Oriol Arteaga, Univ. Barcelona

Light polarization state described by the Stokes Vector

$$S = \begin{bmatrix} I \\ I_x - I_y \\ I_{45^\circ} - I_{-45^\circ} \\ I_+ - I_- \end{bmatrix} = \begin{bmatrix} I \\ Ipcos(2\varphi)cos(2\chi) \\ Ipcos(2\varphi)sin(2\chi) \\ Ipsin(2\varphi) \end{bmatrix}$$

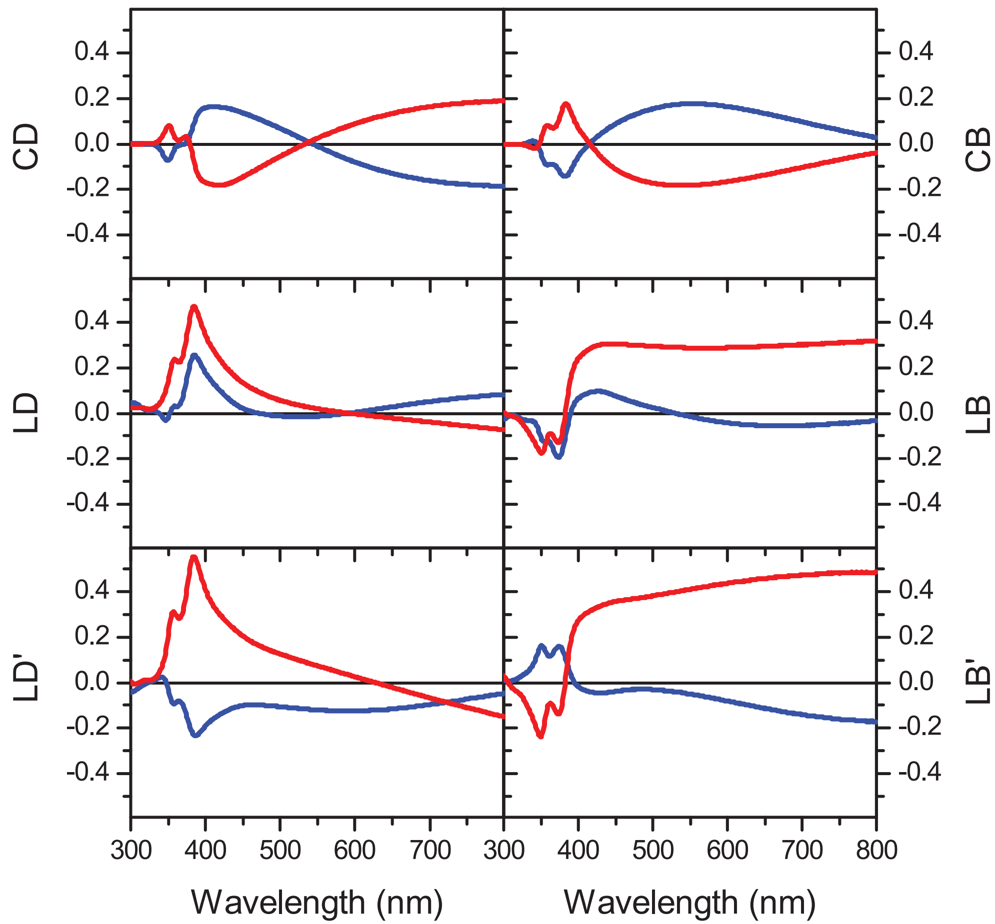


I Intentsity
p Degree of polarization
χ Azimuth
φ Ellipticity

Mueller Matrix describes the sample effect on S_{in}

$$S_{out} = M\ S_{in} \qquad M = \begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix}$$

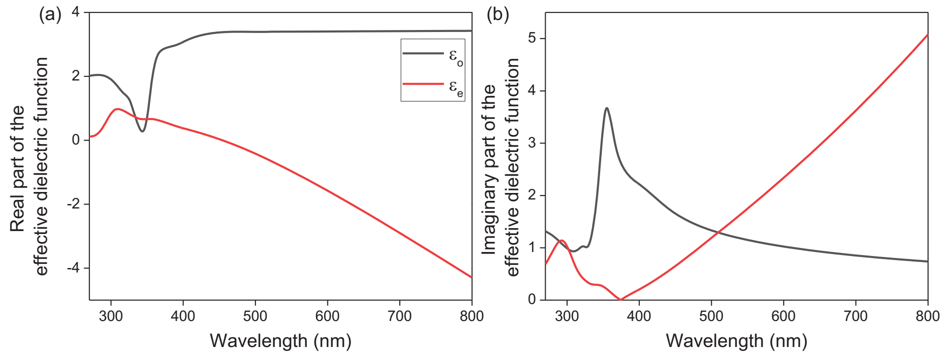
$$M = \exp\begin{pmatrix} A & -LD & -LD' & CD \\ -LD & A & CB & LB' \\ -LD' & -CB & A & -LB \\ CD & -LB' & LB & A \end{pmatrix}$$

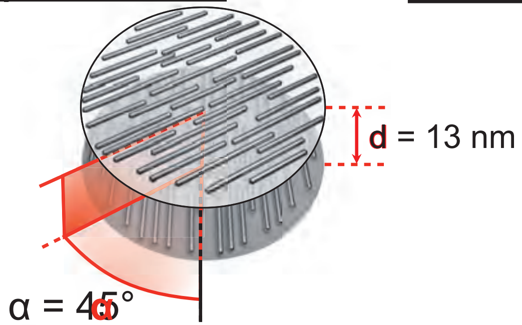


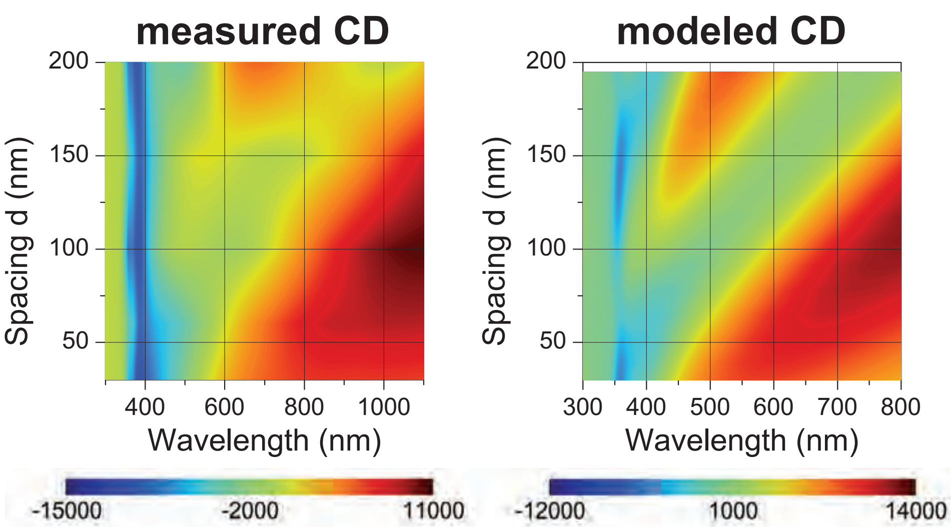
Complex combination of LD, CD, LB, CB

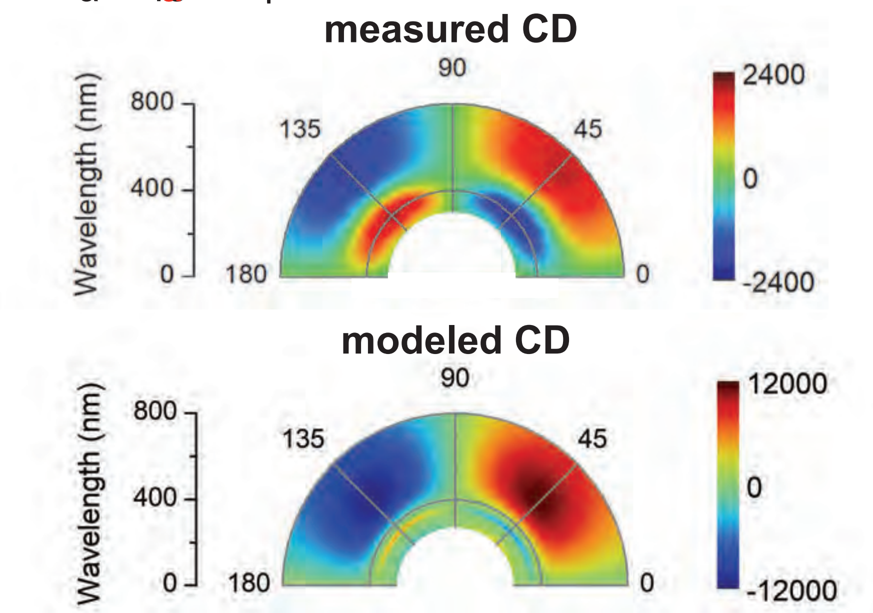
H. Hu et al. *ACS Nano* 2021, *15*, 13653-13661.

Measured effective complex dielectric function → angle α spacing d → Modeled Mueller Matrix → **Modeled LD, CD, LB, CB**





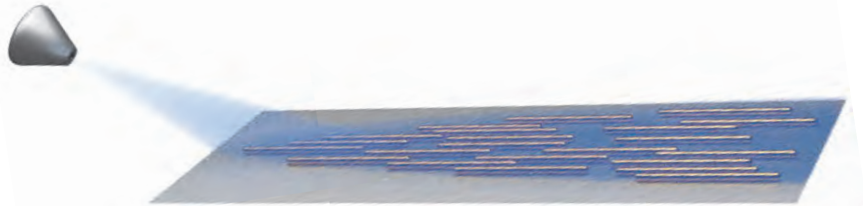


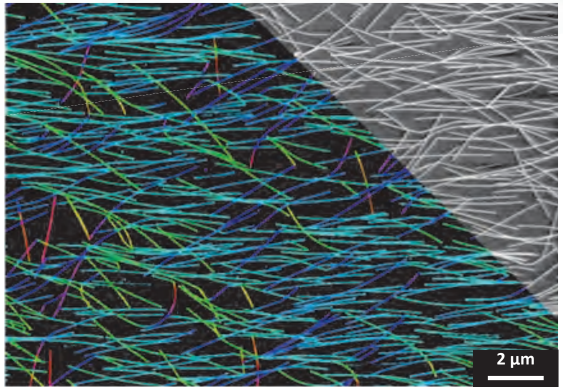


→ Good agreement between measured and modeled properties

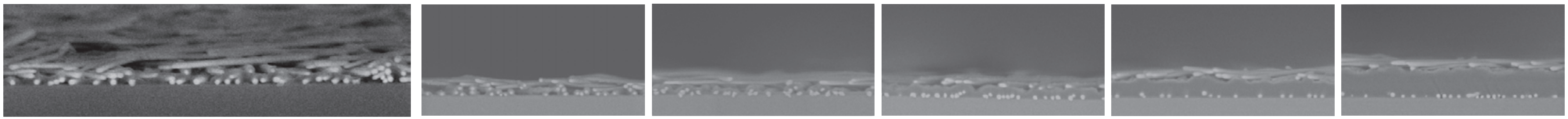
W. Wu et al. *Nano Lett.* 2021, *21*, 8298-8303.

Conclusion





- Grazing Incidence Spraying efficient for **NW and NR orientation**
- Highly **anisotropic optical properties**
- Easy fabrication of large area **chiral metasurfaces**, with structured-dependent **giant circular dichroism**
- Good modeling with a **transfer matrix formalism**
- **Highly versatile approach** (density in plane, number of layers, spacing between layers, choice of material, …)



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SEM: Alain Carvalho

MMP: Yann Battie (U. Lorraine, Metz) and Oriol Arteaga (U. Barcelona)

Modeling: <u>Yann Battie (U. Lorraine, Metz)</u>

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