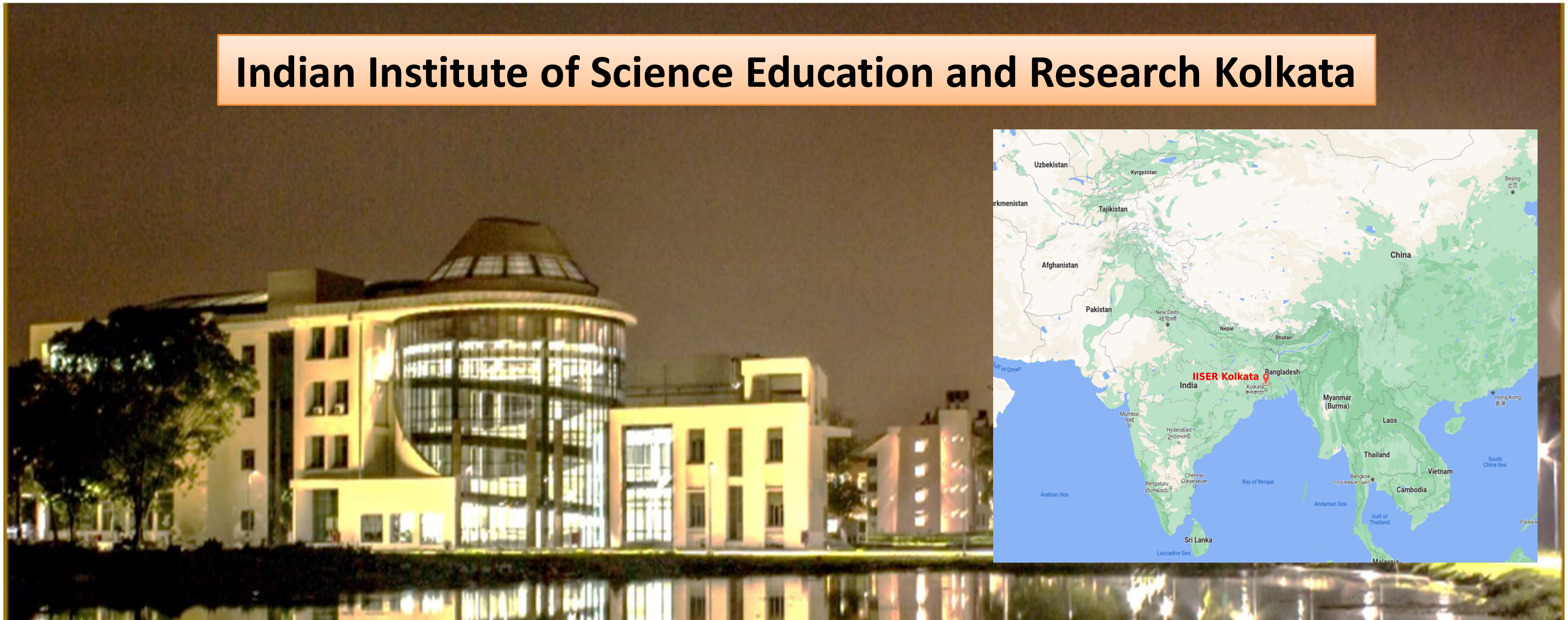
# Polarized light methods for probing sub-wavelength scale structural anisotropy

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**Nirmalya Ghosh**

**Department of Physical Sciences**


**SFM 2022**

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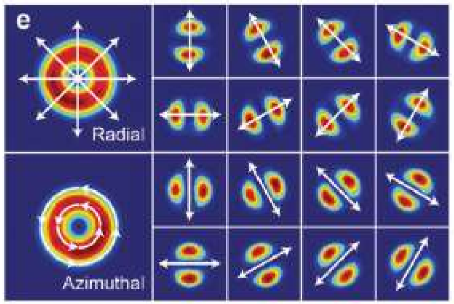
Bio Optics & Nano Photonics

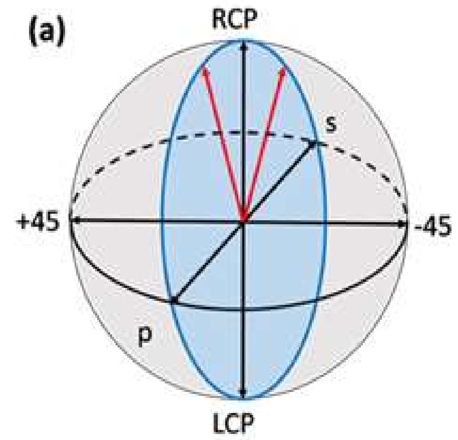
Department of Physical Sciences

# Bio-Optics & Nano - Photonics

## Nano Photonics

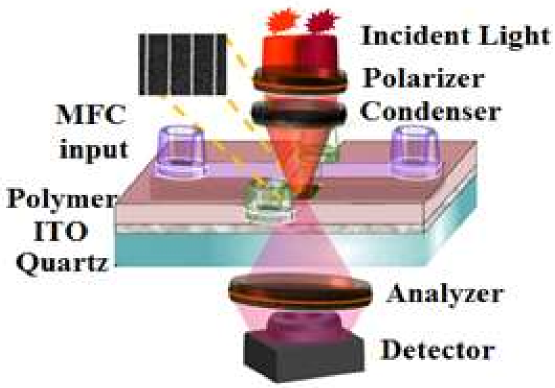
**Polarization & Angular momentum of light**

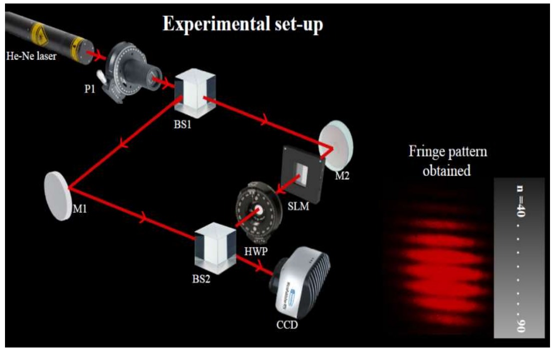



**Spin Orbit interaction of light**

**Plasmonic devices, sensors**

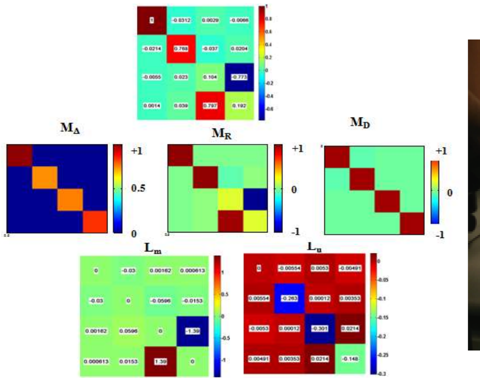


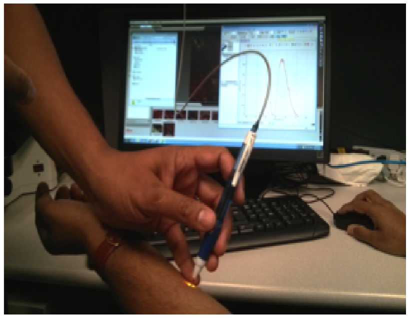




**Space Optics instrumentation**

## Bio-Photonics

**Novel experimental Poalrimetry systems and models for characterization of biological tissues and complex systems**



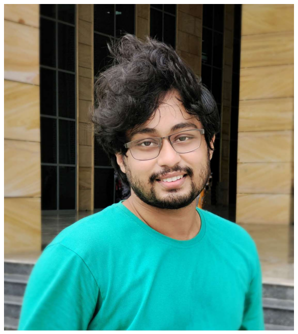



Bio Optics & Nano Photonics

www.iiserkol.ac.in/~nghosh/

## Current PhD students

Niladri Modak



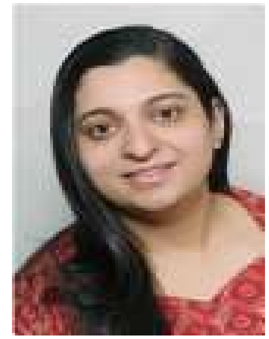
Shyamal Guchhait

Jeeban K Nayak

Anwesha

## Postdoctoral Fellows

Dr. Debdatta Ray



Dr. Tribikram Choudhury

## BS- MS students

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## Former PhD students

Jalpa Soni, Nandan Das, Mandira Pal, Sudipta Saha, Shubham Chandel, Subir K Roy, Ankit K Singh, Athira

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## Collaborators @ Chemistry

Priyadarsi De, C. Malla Reddy, , Raja Shunmugam, Debasish Halder, Debansu Chaudhuri, Soumyajit Roy

**Collaborators from India & abroad**

# Outline

**Probing nano scale structural anisotropy using polarized light**

**The need & the outstanding challenges and issues**

**A unique dark-field polarization Mueller matrix system**

**Simultaneous spectroscopic Mueller matrix + Microscopy & Imaging with sub-wavelength resolution!**

**Differential Mueller matrix inverse analysis**

**Decoupling of confounding effects of high NA polarimetry + Quantitative spatial mapping of anisotropy**

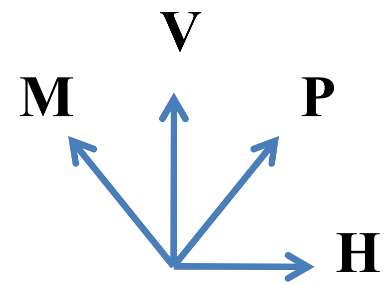
**Probing self-healing behaviour of bio-inspired organic crystals using polarized light**

**Nano scale tissue multifractal anisotropy in polarized light scattering: novel biomarker for precancer detection**

# Stokes-Mueller formalism

## Polarization state of light : Stokes vector     Intensity

$$S=\begin{bmatrix} I \\ Q \\ U \\ V \end{bmatrix}=\begin{bmatrix} E_xE_x^*+E_yE_y^* \\ E_xE_x^*-E_yE_y^* \\ E_xE_y^*+E_yE_x^* \\ i(E_xE_y^*-E_yE_x^*) \end{bmatrix}=\begin{bmatrix} E_{0x}^2+E_{0y}^2 \\ E_{0x}^2-E_{0y}^2 \\ 2E_{0x}E_{0y}\cos\delta \\ 2E_{0x}E_{0y}\sin\delta \end{bmatrix}=\begin{bmatrix} I_H+I_V \\ I_H-I_V \\ I_{45}-I_{135} \\ I_R-I_L \end{bmatrix}$$




## Degree of polarization

$$DOP=\frac{\sqrt{Q^2+U^2+V^2}}{I}$$

| Unpolarized state | Horizontal polarization ($0^0$) | Vertical polarization ($90^0$) | $+45^0$ polarization | $135^0$ ($-45^0$) polarization | Left circular polarization | Right circular polarization |
|---|---|---|---|---|---|---|
| $\begin{pmatrix}1\\0\\0\\0\end{pmatrix}$ | $\begin{pmatrix}1\\1\\0\\0\end{pmatrix}$ | $\begin{pmatrix}1\\-1\\0\\0\end{pmatrix}$ | $\begin{pmatrix}1\\0\\1\\0\end{pmatrix}$ | $\begin{pmatrix}1\\0\\-1\\0\end{pmatrix}$ | $\begin{pmatrix}1\\0\\0\\-1\end{pmatrix}$ | $\begin{pmatrix}1\\0\\0\\1\end{pmatrix}$ |

# Quantitative Polarimetry -Stokes-Mueller formalism

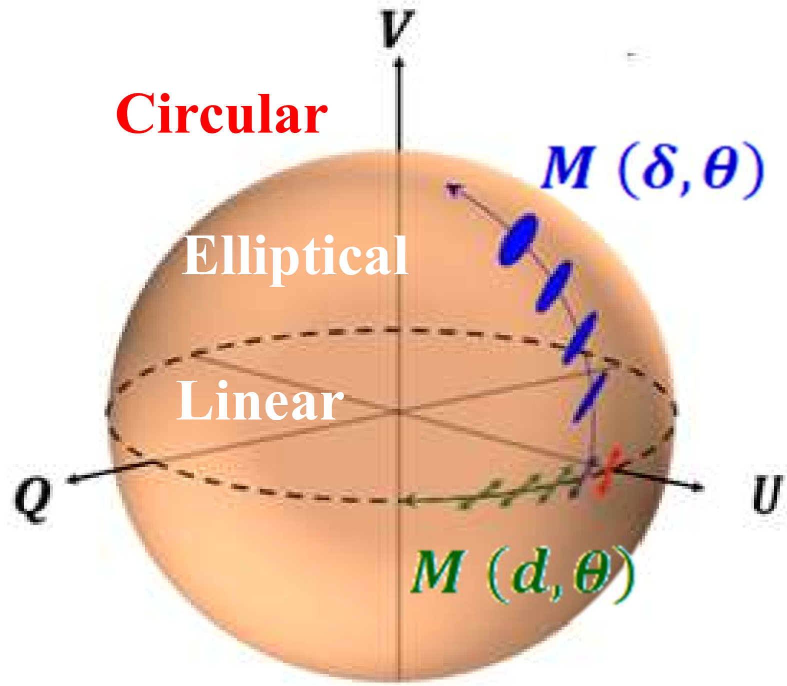
## Mueller matrix

Transforms Stokes vector of incident light to that of scattered light

**Complete information about all the anisotropy properties of medium**

$$S_0 = MS_i$$

$$\begin{bmatrix} I_o \\ Q_o \\ U_o \\ V_o \end{bmatrix} = \begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \begin{bmatrix} I_i \\ Q_i \\ U_i \\ V_i \end{bmatrix}$$




**Phase anisotropy**
Retardance - δ

**Orientation of anisotropy axis θ**

$$\theta = \frac{1}{2} tan^{-1}\left(\frac{m_{24}}{m_{34}}\right)$$

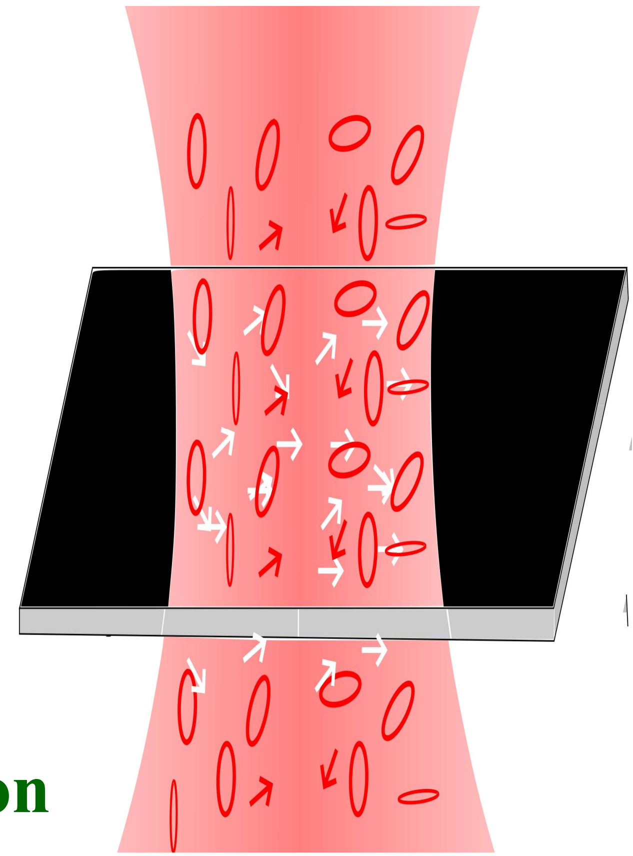
$$\theta = \frac{1}{2} tan^{-1}\left(\frac{m_{13}}{m_{12}}\right)$$

**Amplitude anisotropy**
Diattenuation - d

**Depolarization Δ**

# Challenges in nano-sensitive Polarimetry

**Anisotropy parameters measurement with nanometer spatial resolution (High NA imaging, NA ~ 0.9)**



○**Non-ideal POL behaviour:** Scrambling of polarization due to **tight focusing**

Confounding effects– Crosstalk +Blurring

Difficulties in interpretation & quantification

○ Difficulties in recording **weak polarization scattering signal of nano scale objects**

**Custom designed dark-field Mueller matrix microscopy system** + **Robust calibration** + **Polarization inverse analysis model**

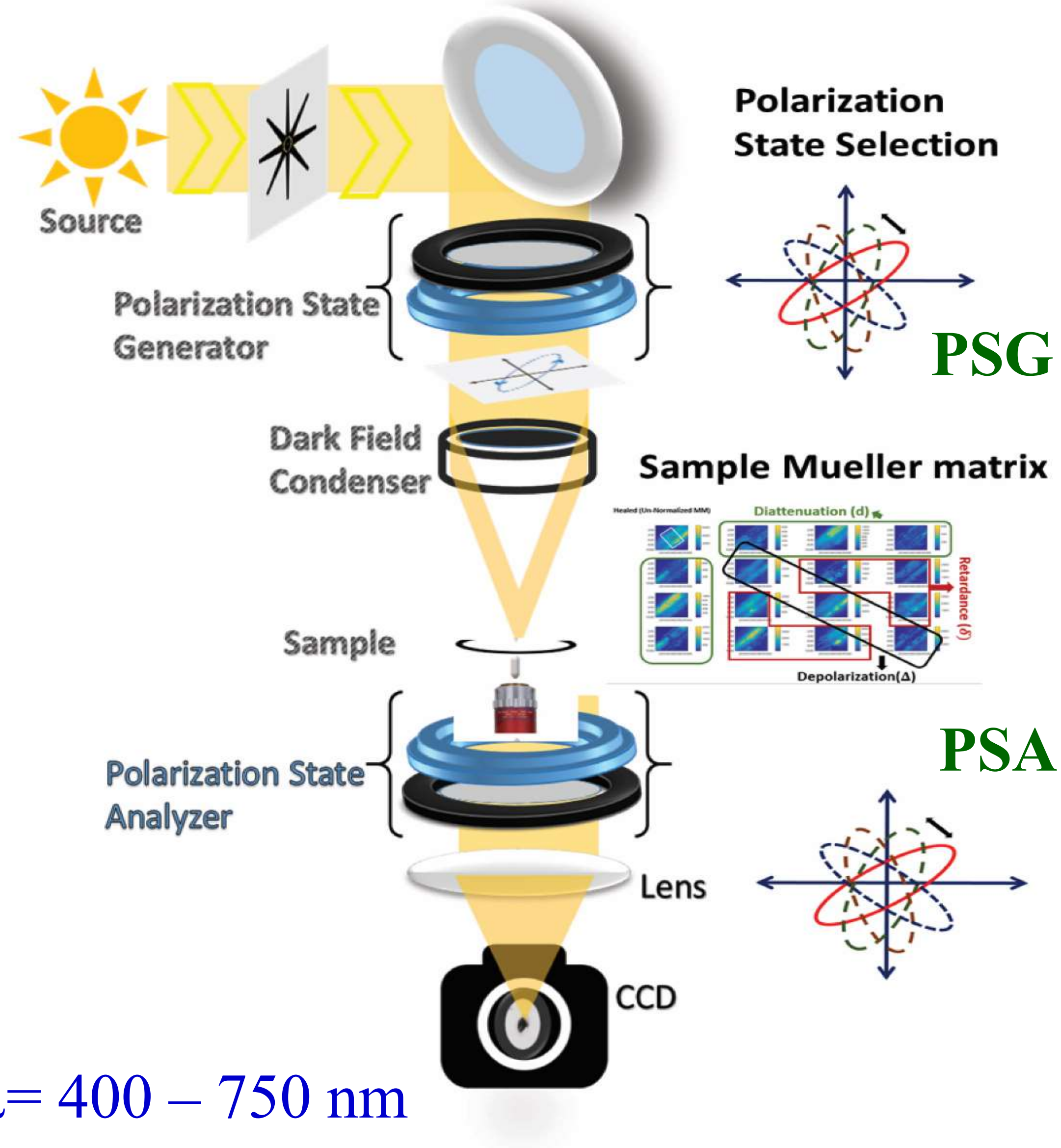
# Mueller matrix measurements integrated with Dark-field microscope + Spectroscopy

**Generation & Analysis of 4 optimized elliptical polarization states**

**Mueller matrix Spectroscopy + Imaging!**

**Developed in-house**

Applied Phys. Lett., 104, 131902 (2014), Sc. Rep, 6, 26466 (2016), Opt. Lett., 39, 2431 (2014), Opt. Exp, 21, 15475 – 15489 (2013 )




$\lambda = 400 – 750$ nm

# Scheme for Mueller matrix construction

4x4 intensity measurement matrix $M_i$ & the Mueller matrix $M_s$

$$\boldsymbol{M_i = A\, M_s\, W}; \qquad \boldsymbol{M_s = A^{-1}\, M_i\, W^{-1}}$$

**PSG matrix *W***

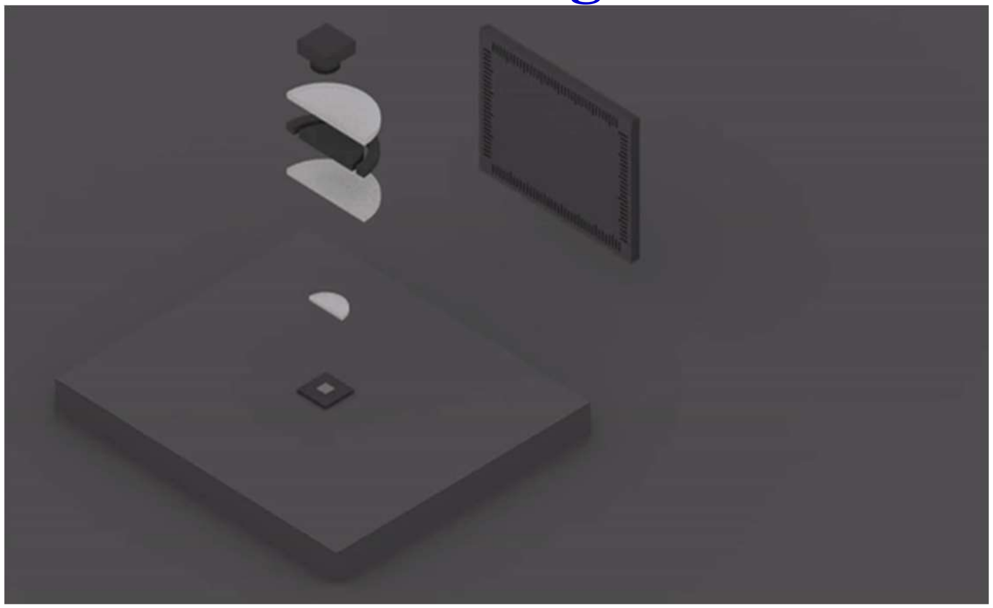
**PSA matrix *A***

Experimental $W(\lambda)$ and $A(\lambda)$ determined using a **robust calibration method**

**Takes care of the complicated polarization evolution due to tight focusing & ensures high sensitivity**

**Decoupling of confounding effects: Polarization inverse analysis**

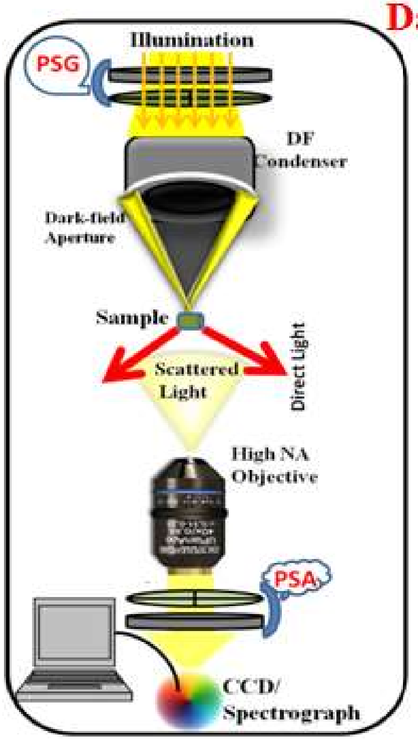
# Dark field arrangement enables detection of weak scattering signal from nano scale objects



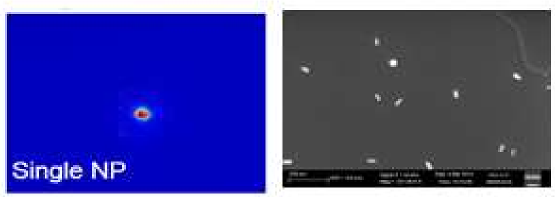
Capable of

- ✓ Spectral measurements
- ✓ Microscopy
- ✓ Full 16-element Mueller matrix

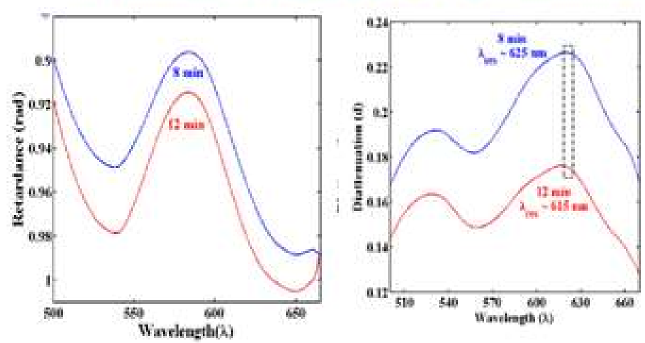
<u>all from single isolated nano-particle</u>



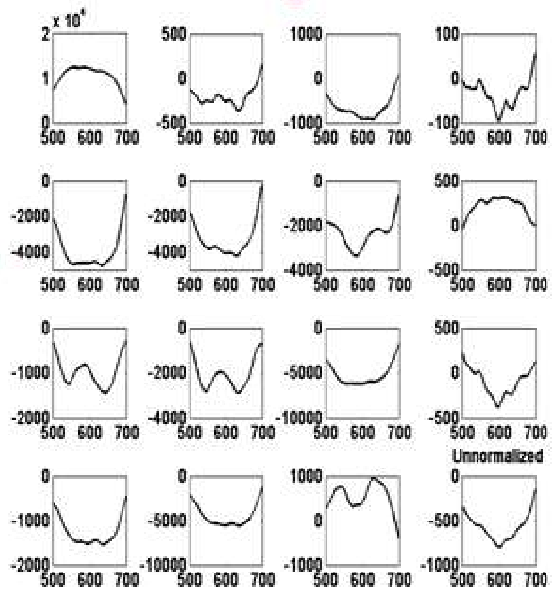

Dark field & SEM image of Au nano-rod




Spectral Polarization parameters



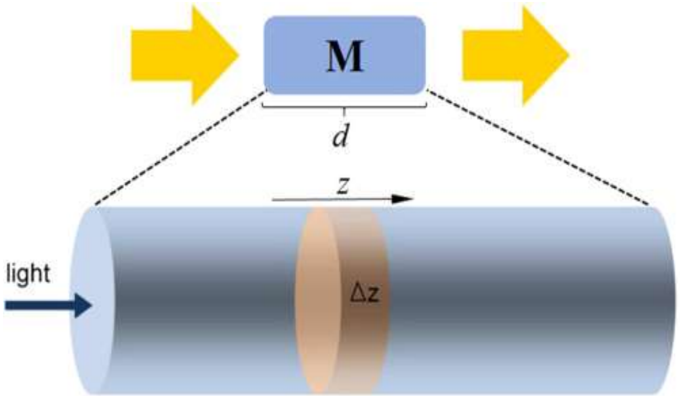

Full spectral Mueller matrix from a single nano-rod



# Decoupling of POL effects: Differential Mueller matrix formalism

## Adaptation of differential Jones calculus to depolarizing Mueller matrix

R. C. Jones, J. Opt. Soc. Am. 38, 671 (1948)




$$\frac{d\mathbf{M}(z)}{dz} = \mathbf{m}\mathbf{M}(z)$$

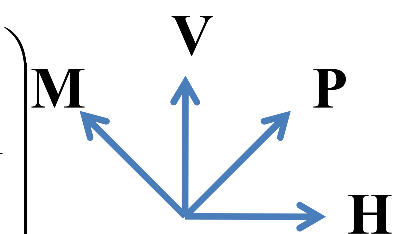
$$\frac{dM}{dz} = mM$$

**LD/CD: Linear / Circular diattenuation**

**LR/CR: Linear / Circular retardance**

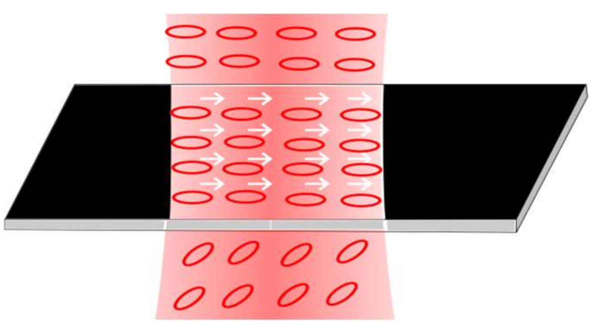
**Ideal ordered system (Anti-symmetric form)**

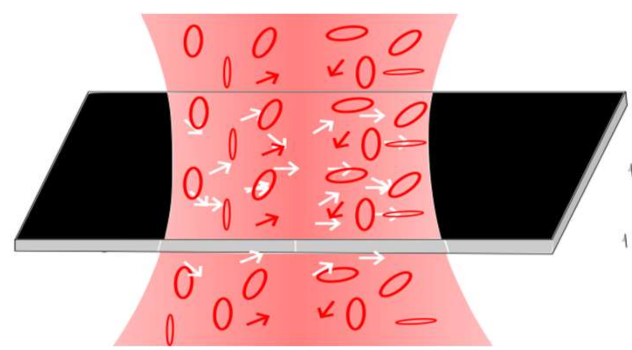
$$m=\begin{pmatrix} \alpha & LD_{HV} & LD_{PM} & CD \\ LD_{HV} & \alpha & CR & LR_{PM} \\ LD_{PM} & -CR & \alpha & LR_{HV} \\ CD & -LR_{PM} & -LR_{HV} & \alpha \end{pmatrix}$$



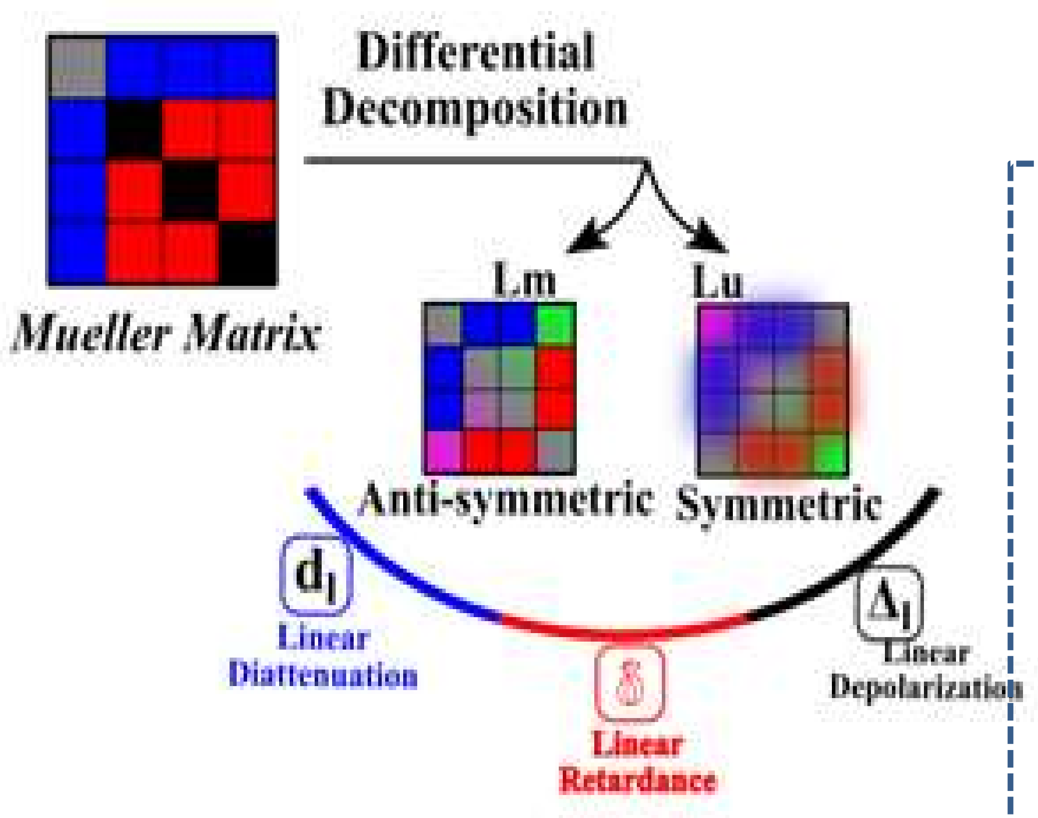

**Non-ideal POL response, depolarization + disorder**

$$m^{/} = \begin{pmatrix} \alpha & LD_{HV} & LD_{PM} & CD \\ LD^{/}{}_{HV} & \alpha_1 & CB & LB_{PM} \\ LD^{/}{}_{PM} & -CB^{/} & \alpha 2 & LB_{HV} \\ CD^{/} & -LB^{/}{}_{PM} & -LB^{/}{}_{HV} & \alpha_3 \end{pmatrix}$$





# Decouple the non-ideal POL response using the symmetries of Mueller matrix




J. Biomed. Opt., 17, 105006 (2012)
Ossikovsky, Opt. Lett., 32, 348 (2015)
Phys Rev. A, 103, 053518 (2021)

## Quantification of anisotropy

**Linear retardance**

$$\delta = \sqrt{[L_m(2,4)]^2 + [L_m(3,4)]^2}$$

$$\theta = \frac{1}{2} tan^{-1}\left(\frac{L_m(2,4)}{L_m(3,4)}\right)$$

**Linear diattenuation**

$$\mathrm{d} = tanh\left(\sqrt{[L_m(1,2)]^2 + [L_m(1,2)]^2}\right)$$

**Depolarization**

$$\Delta = \frac{1}{3}[L_u(2,2) + L_u(3,3) + L_u(4,4)]$$

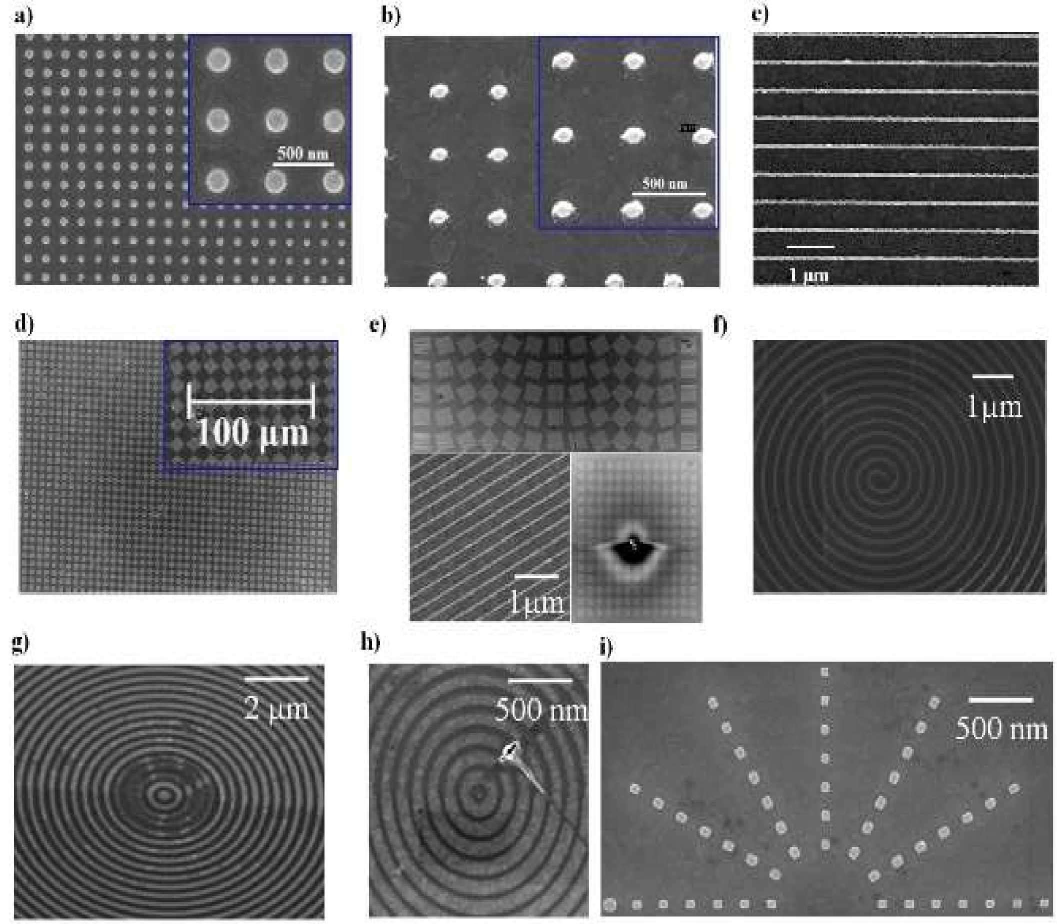
- **Non-ideal POL response due to tight focusing filtered out through $L_u$**
- Quantitative information on structural order : anisotropy parameters in $L_m$

# Anisotropy imaging with nano-scale spatial resolution confirmed!

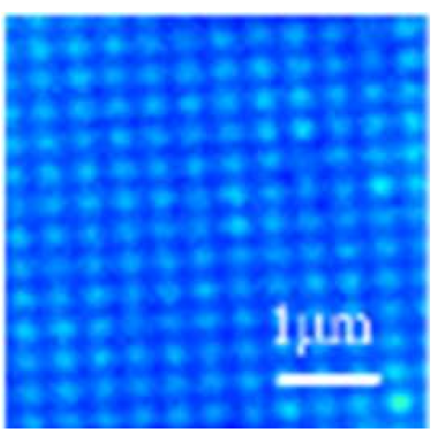
**Nanostructured anisotropic medium – Plasmonic (Gold - Au) metasurfaces**

**Electron beam Lithography**

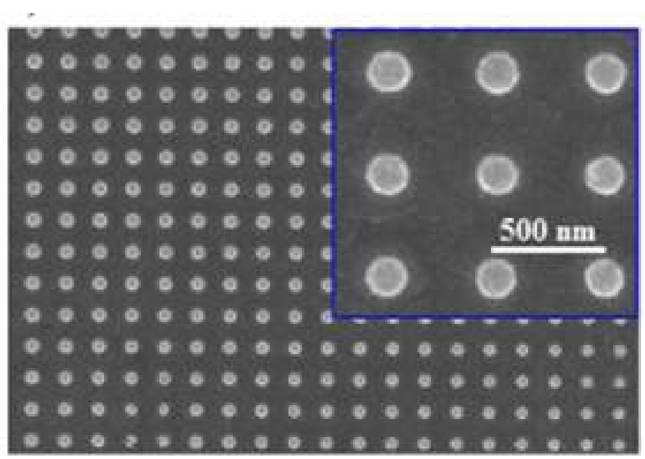
**Tailoring Geometry at nanometer length scale**




**Dark field POL $M_{11}$**




**SEM**




**Resolution**

$$\frac{\lambda}{2\,NA} \sim 300\ nm$$

*ACS Nano*, 11, 1641-1648 (2017), Communications Physics, 4, 102 (2021), *Phys. Rev. A., 97, 053801 (2018), Phys. Rev. A., 97, 043823 (2018)*

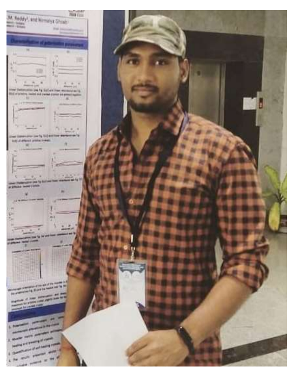
# Application Example - 1

## Probing self-healing behaviour of piezoelectric molecular crystals using polarized light

**Gaining quantitative insight on the self-healing mechanism through the *microscopic* optical anisotropy parameters**

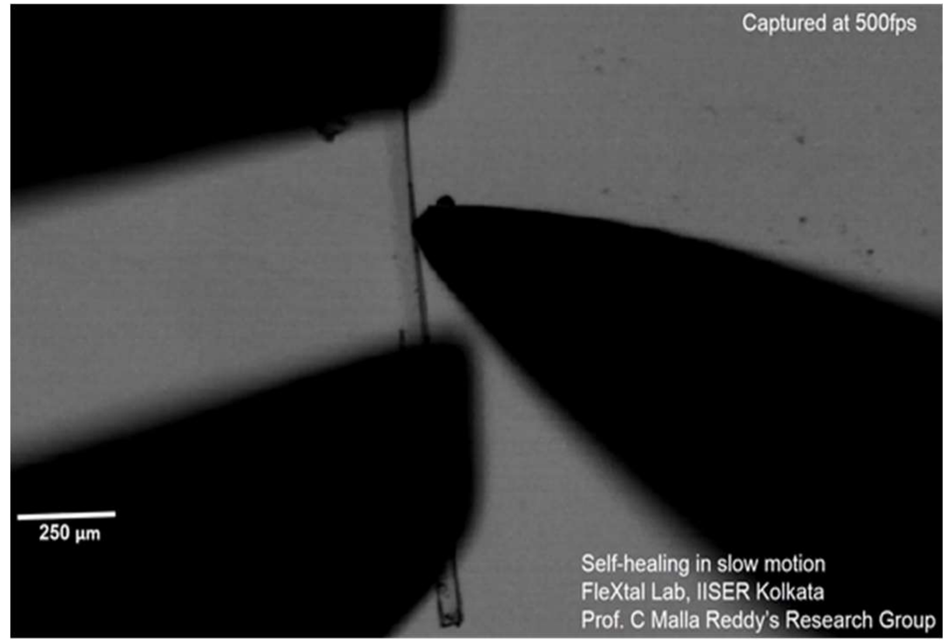
Bhunia *et al.*, Science, 2021, 373, 6552, 321-327

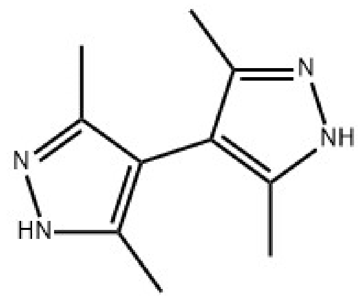




**Dr. C. Malla Reddy: CMR group, DCS, IISER Kolkata**

# Autonomous Self-repair in Piezoelectric Molecular Crystals

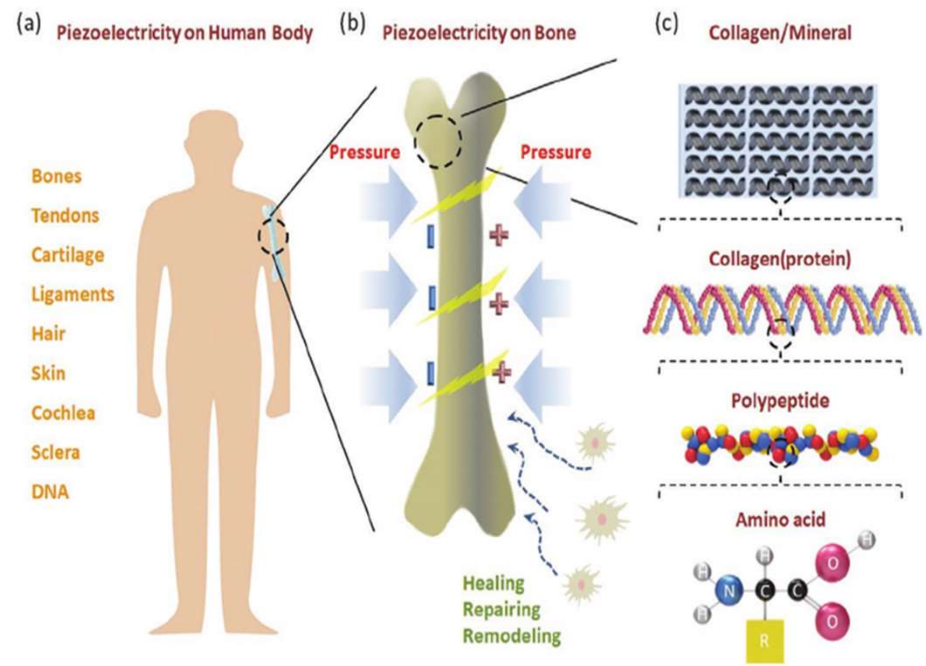
**Bipyrazole molecular crystal**

**First demonstration of autonomous self-healing in crystalline materials - No external stimuli, diffusion-less, Fast (~ ms)**

**Polarization studies unraveled the Piezoelectric origin of the self-healing mechanism of the Polar crystal**

**Bhunia *et al.*, Science, 2021, 373, 6552, 321-327**

# Self-healing in nature (bone) – provides a clue



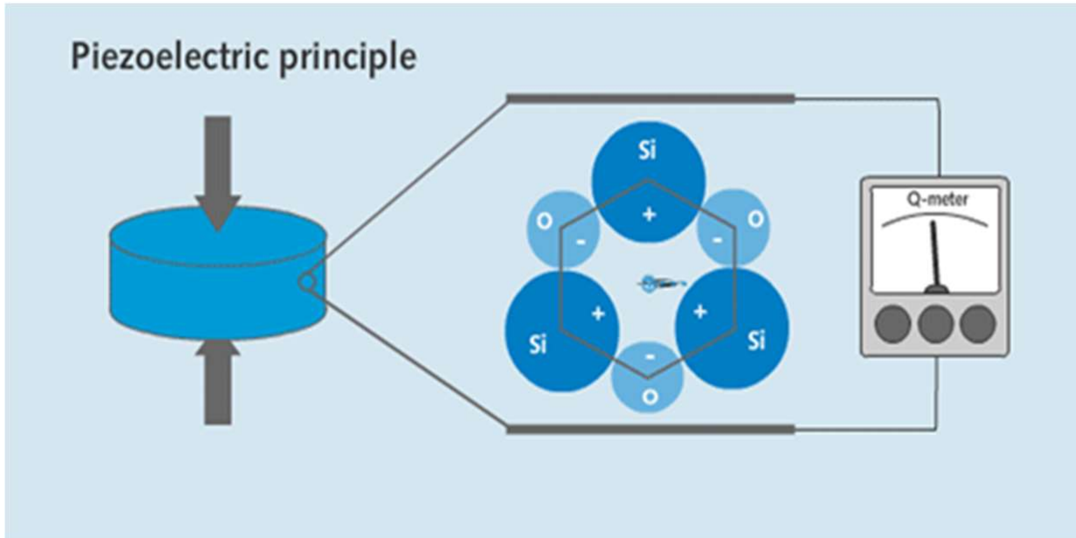

Stress acting on the bone creates an electric potential, and attracts osteogenic cells due to the formation of electric dipoles. It subsequently accumulates minerals, mainly calcium, on the compression side of the bones

Basic building blocks of bone is collagen, which is **piezoelectric** in nature because of its noncentrosymmetric structure made of polypeptides

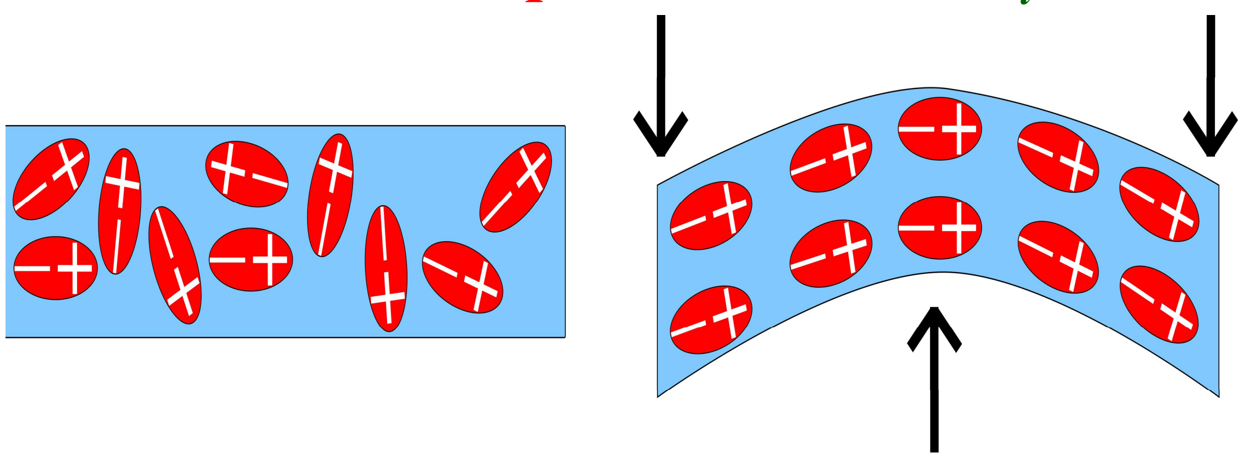
Fabian Vasquez-Sancho et. al Adv. Mater. 2018, 30, 1705316

Video source: https://www.youtube.com/watch?v=EBPYSMH5OGo

# Piezoelectric response of non-centrosymmetric Polar crystals




**Stress-induced changes in the permanent dipoles leading to *macroscopic* Polarization $P_i$**



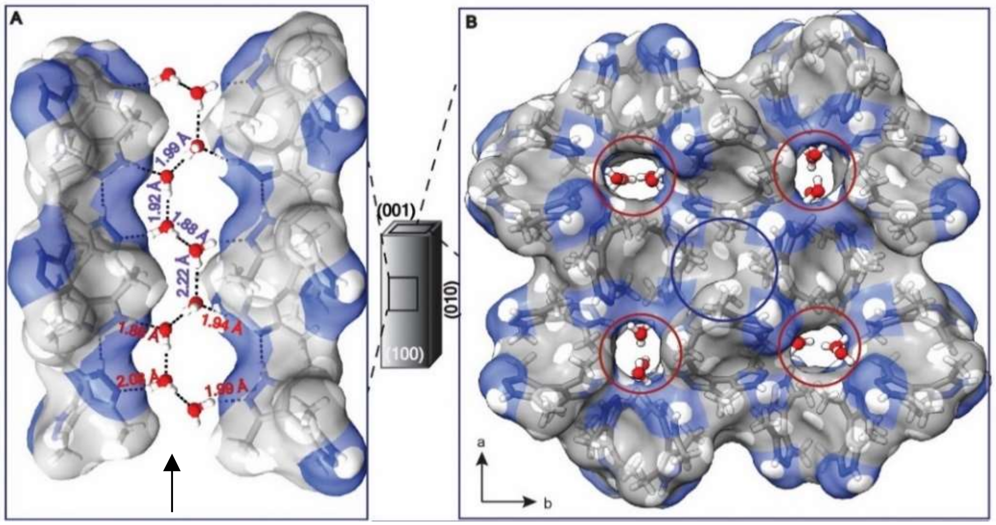
Task: Probe changes in the ***macroscopic*** Polarization (**Piezoelectric response**) through **stress-induced** changes in ***microscopic*** optical anisotropy

# Polarized light for probing structural anisotropy in crystals

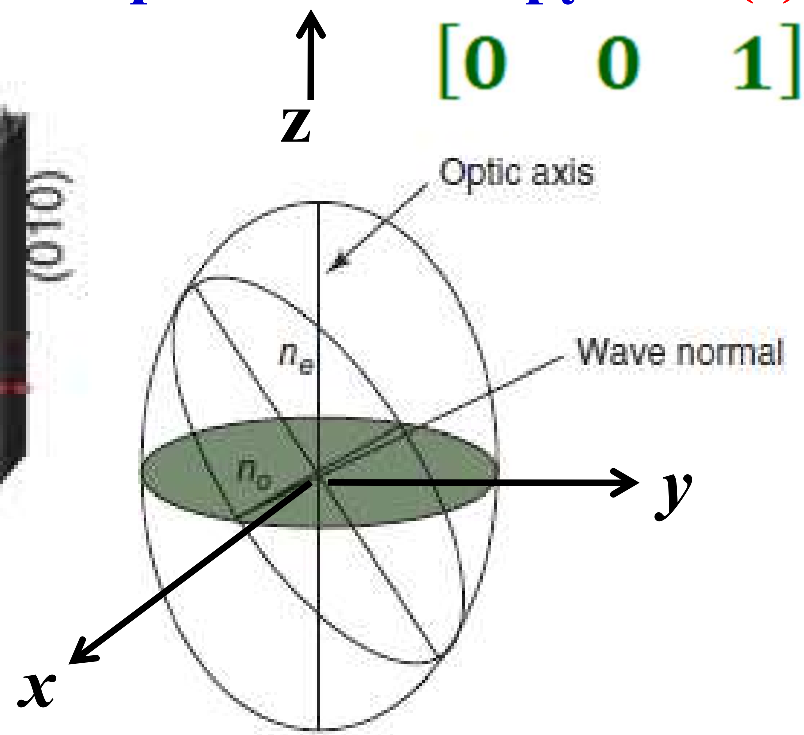
**Bipyrazole Polar crystal**

**Tetragonal unit cell**

**Optical anisotropy axis (c)**









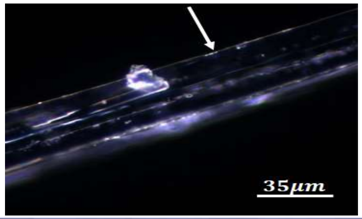
$n_x = n_y \neq n_z$ **uniaxial anisotropy of the *microscopic* building blocks**

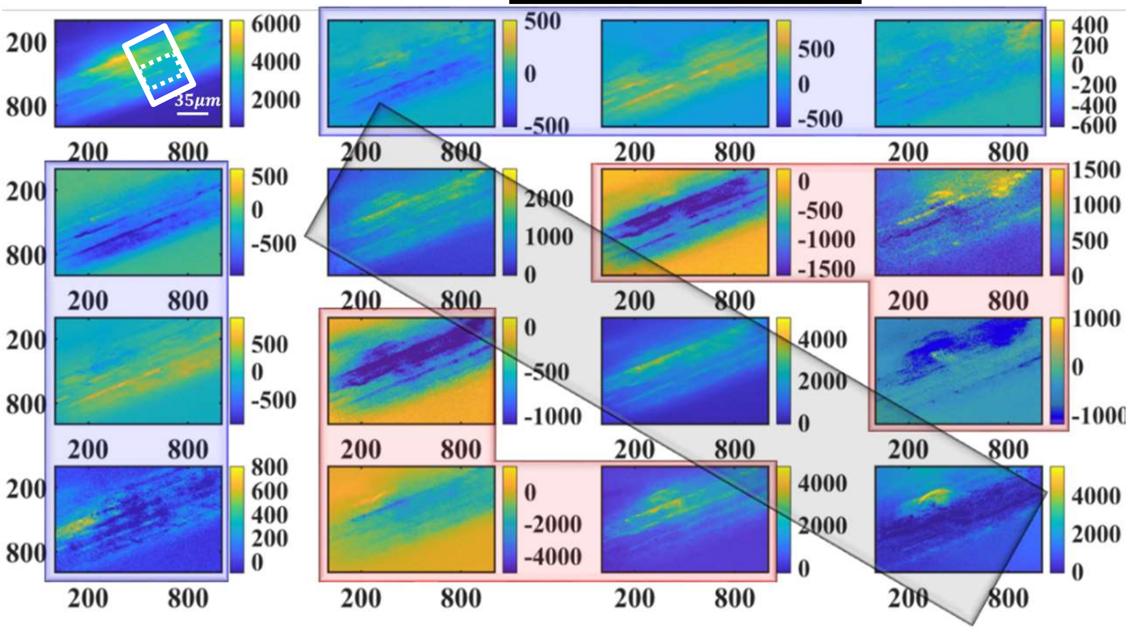
**Optical anisotropy axis** ⟷ **Polar axis (c)**

**Linear uniaxial anisotropy fits Stokes-Mueller formalism**

# Manifestation of structural anisotropy in Mueller matrix

## Healed crystal



**Structural anisotropy:**

**Symmetries of MM elements**

**Blurred**

**Amplitude (diattenuation) &**

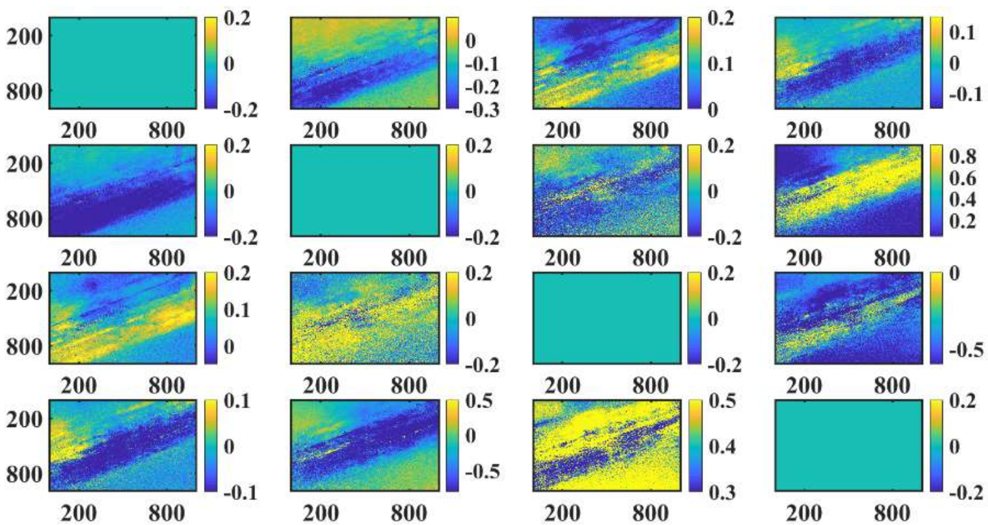
phase anisotropy (retardance) -

**Crosstalk**

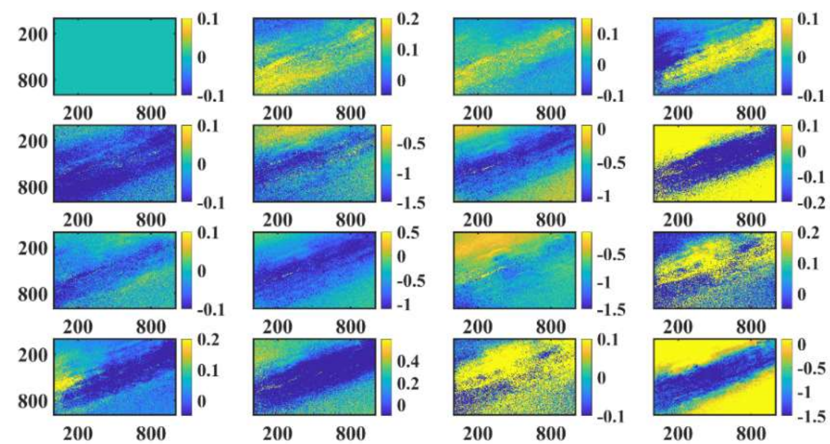
**Depolarization-** tight focusing

Confounding effects decoupled – ***microscopic* anisotropy** in $L_m$

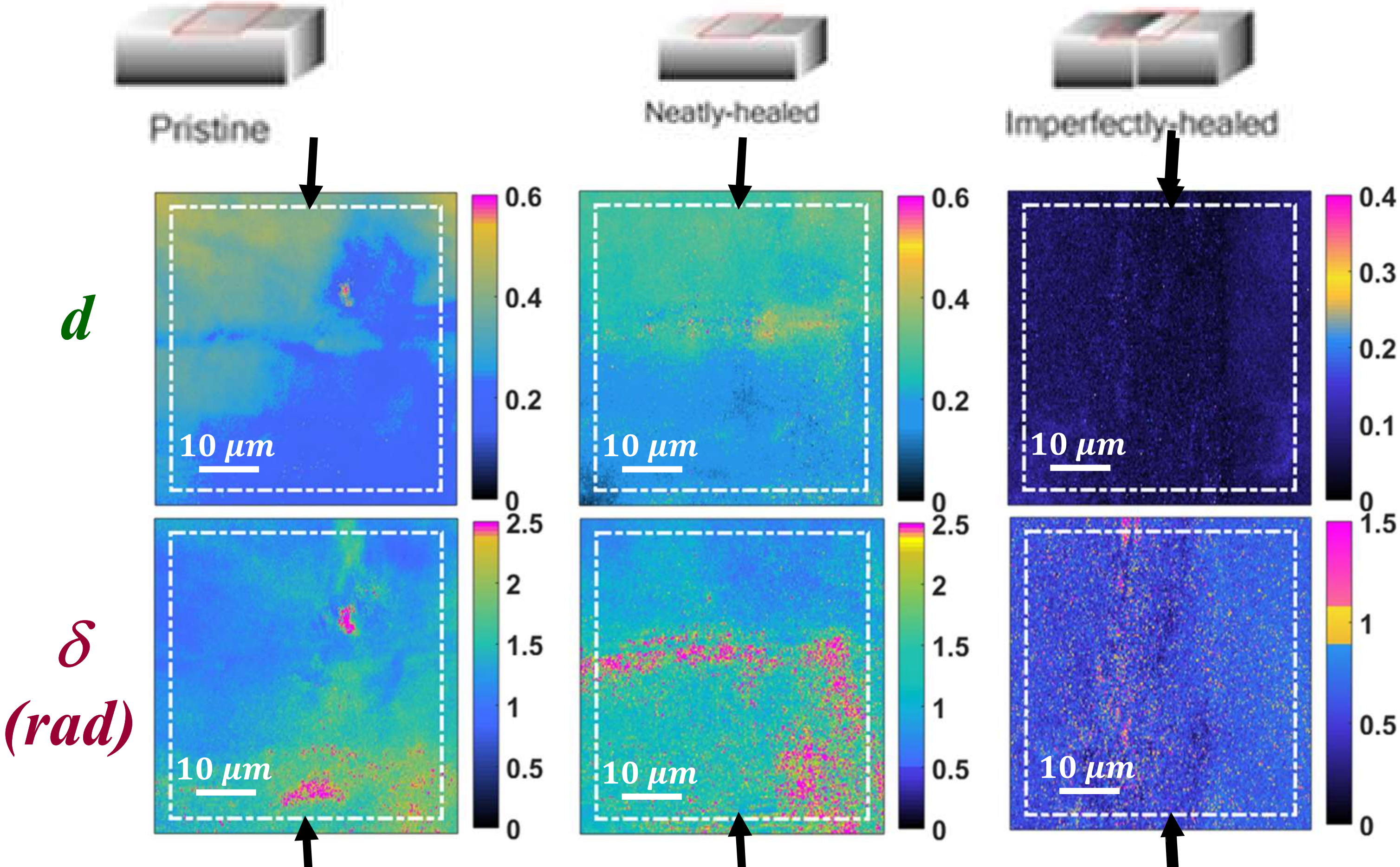
**Lm *matrix***



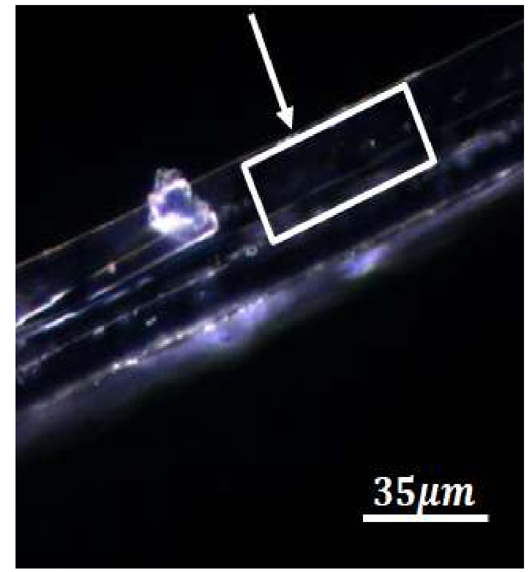
**Lu *matrix***



# *Microscopic* structural anisotropy parameters




**Anisotropy parameters with sub-micron resolution**




Homogeneous region of interest

Pristine crystal– high d and δ

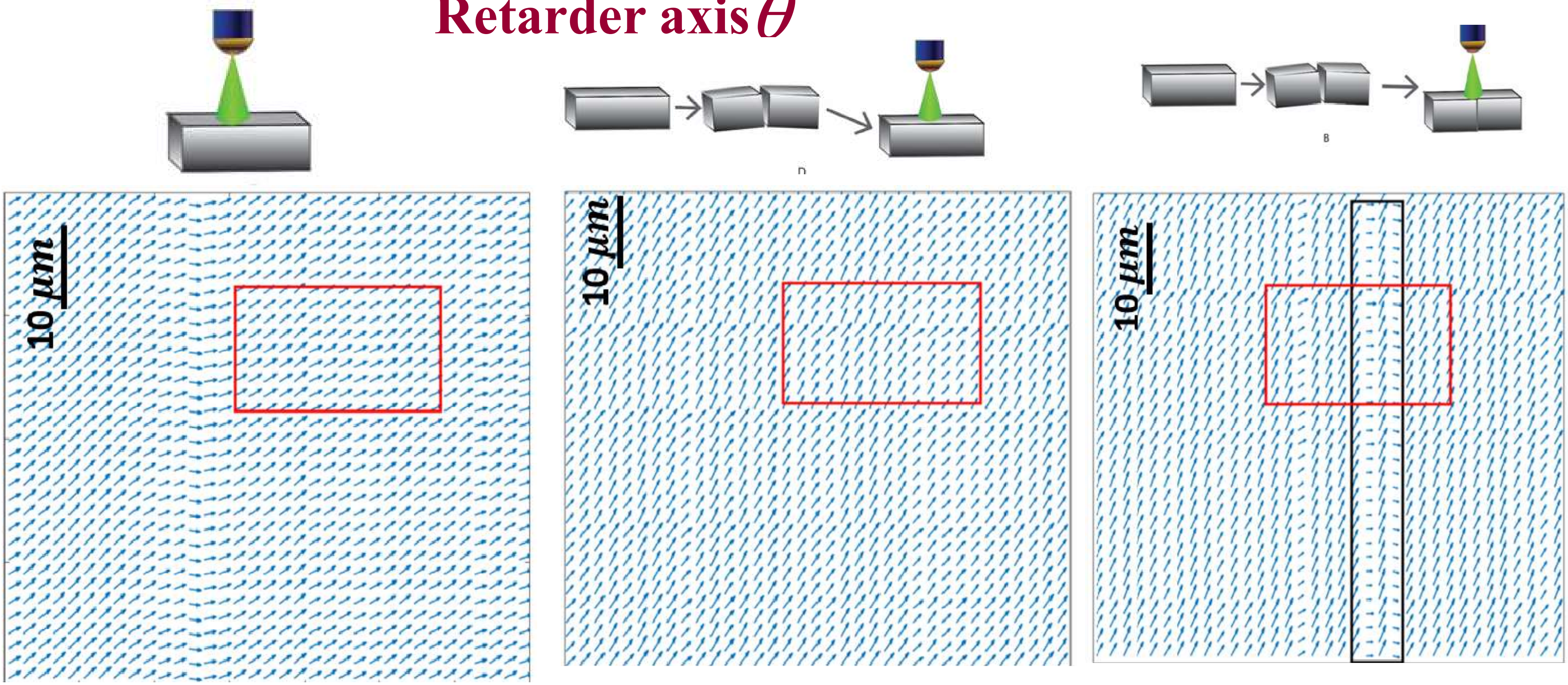
High degree of structural order in the microscopic anisotropy units

d and δ of healed marginally lower than pristine: Self-healing (~ 85%)

Imperfectly-healed : Significantly lower magnitudes of d and δ

# Microscopic orientation of the anisotropic units

Retarder axis $\theta$




Pristine and **neatly-healed**:

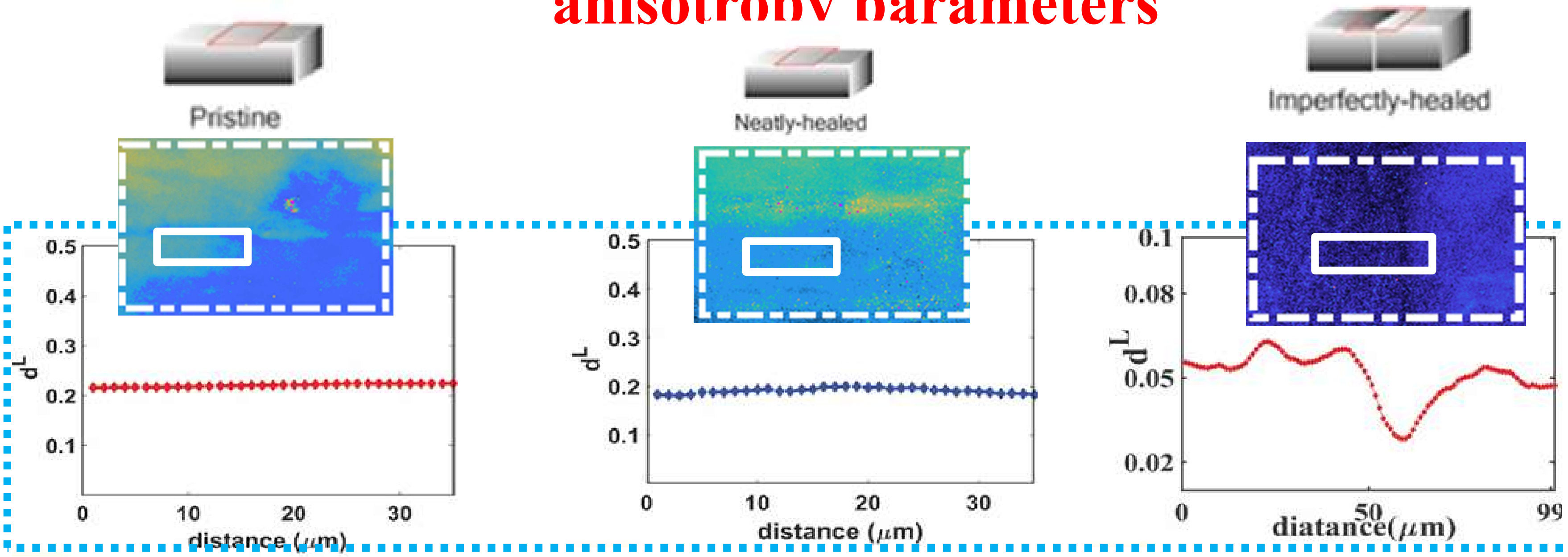
**Orientational order in the nanoscopic building blocks**

Repair with nanoscopic precision & long range crystalline order

Imperfectly-healed crystals: Orientational disorder at the crack junction

**Science, 2021, 373, 6552, 321-327**

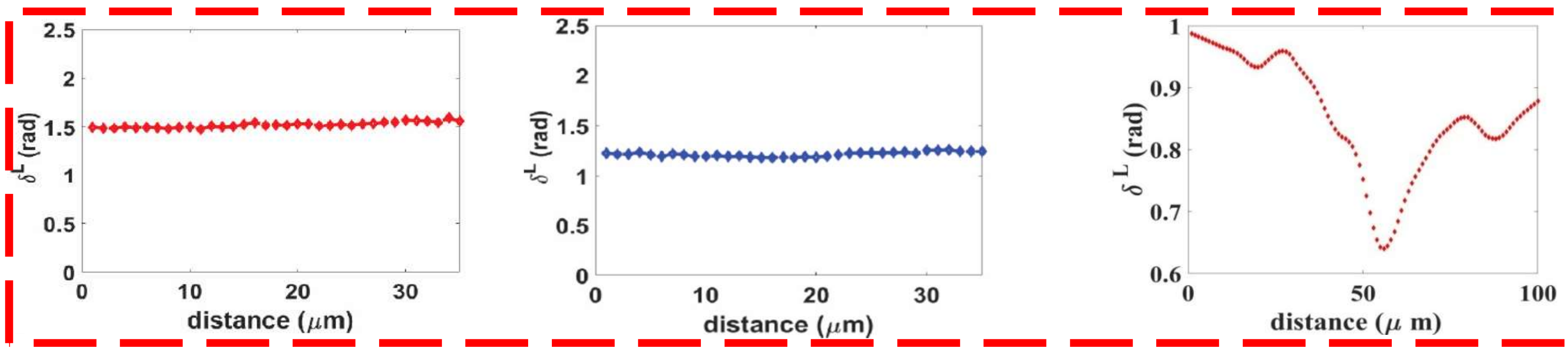
# Quantitative assessment of healing through structural anisotropy parameters




$d^L$~ 0.22 ± 0.03

$d^L$~ 0.18 ±0.03

$d^L$~ 0.07±0.02




$\delta^L$~ 1.52 ± 0.30

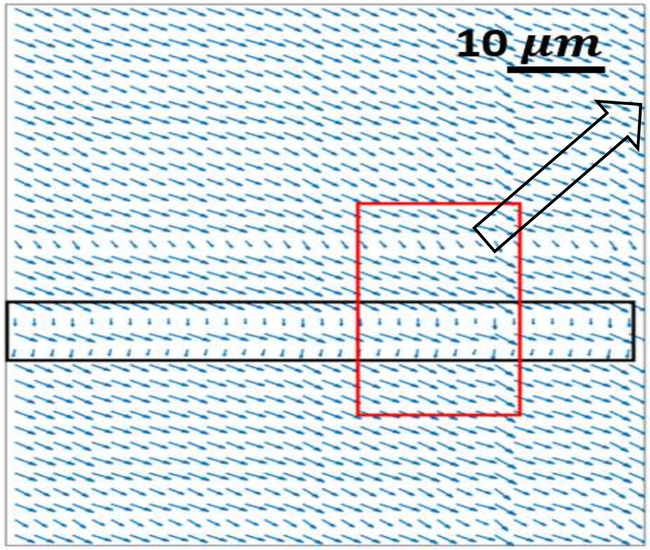
$\delta^L$~ 1.32 ± 0.15

$\delta^L$~ 0.80 ± 0.20

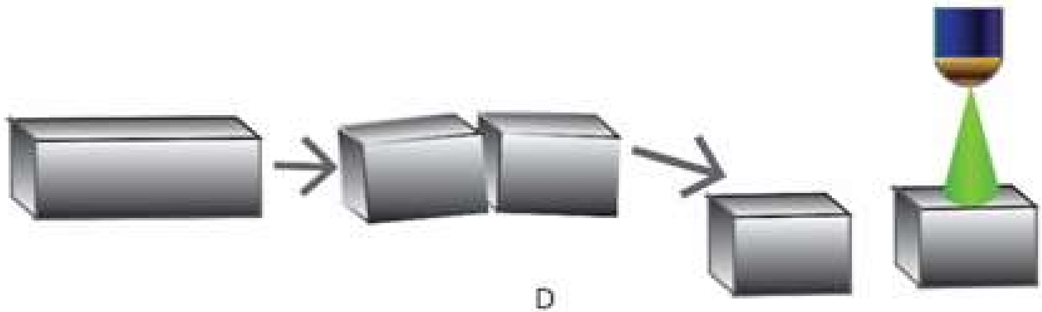
**Self-healing efficiency in the neatly-healed crystals ~ 85%**

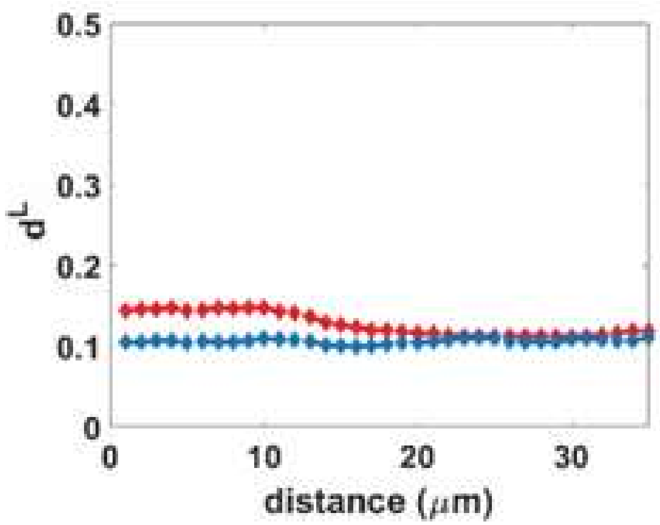
**~ 60% decrease in the microscopic anisotropy for imperfect healing**

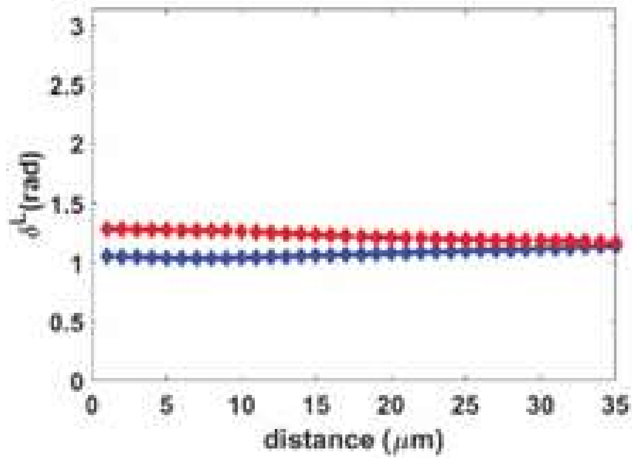
# Large reduction in *microscopic* anisotropy  for imperfect healing




Spatial averaging with randomly oriented / misaligned anisotropic domains




***d* & *δ*** ↓

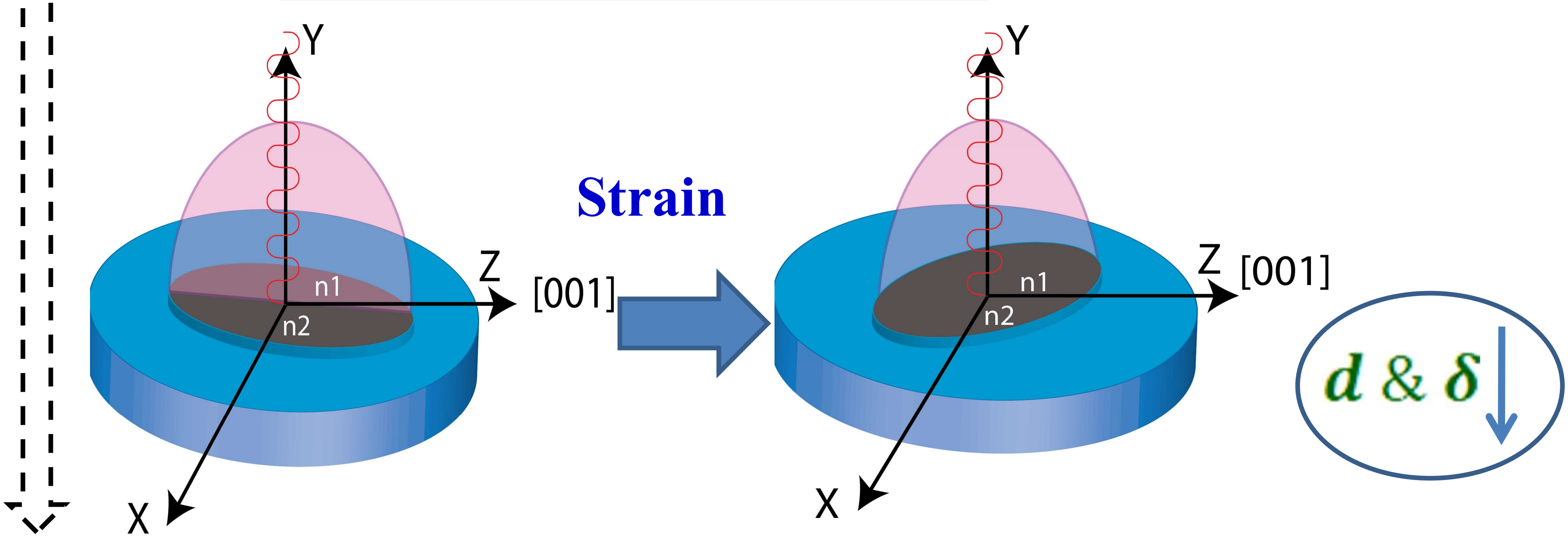
**Fragmented crystal: Lower magnitudes of microscopic anisotropy ~ 30 % reduction**

# Insight on the healing mechanism

**Reduction in anisotropy of fragmented crystal**

Decrease in structural order in the *microscopic* building units due to strain **(Plasticity) or permanent defects-** mechanical stress

**Photo-elastic effect**

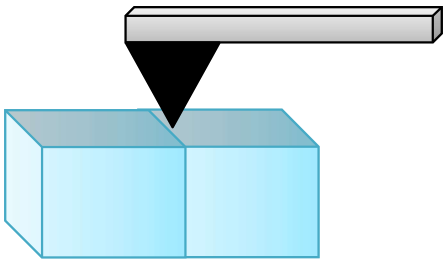


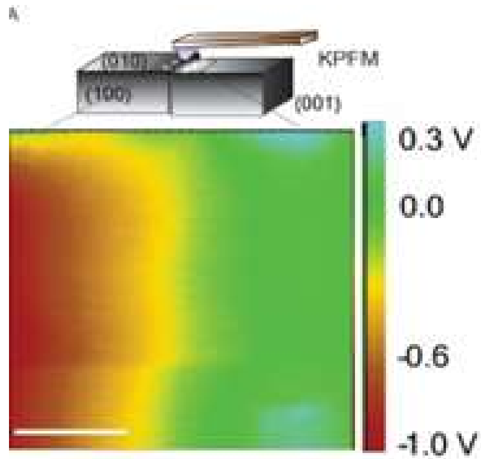

Change in permanent dipoles or ***macroscopic*** polarization **P** - **piezoelectric effect**

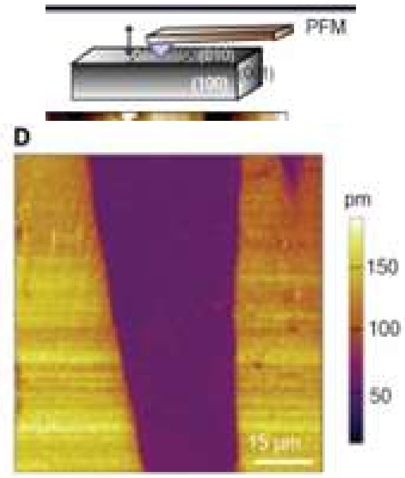
**Surface charges** on the fractured faces

# Insight from Polarization studies

Generation of **surface charges** through **Piezoelectric effect**






**Confirmed by Kelvin probe & Piezo Force microscopy**

**Science, 2021, 373, 6552, 321-327**

- Efficient healing: Release of strain & restoration of **native anisotropy**

  Efficiency quantified through *microscopic* anisotropy parameters

- Inefficient healing : Penalty in structural order, Enhanced residual stress. **Alignment with crystallographic precision is favorable**

# Application Example - 2

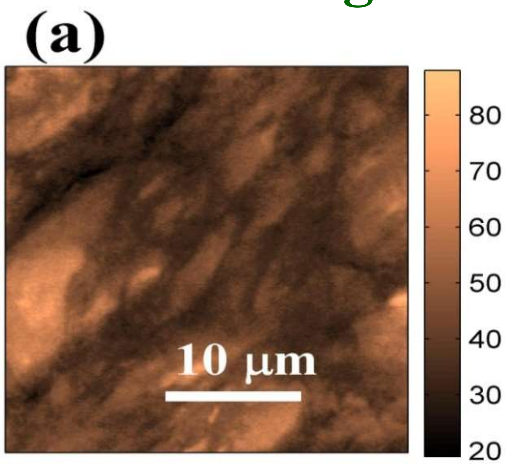
## Nano scale tissue multifractal anisotropy in polarized light scattering: novel biomarker for precancer detection

**Nanometer scale tissue structural anisotropy probed via multifractal analysis of wavelength variation of Mueller matrix elements**

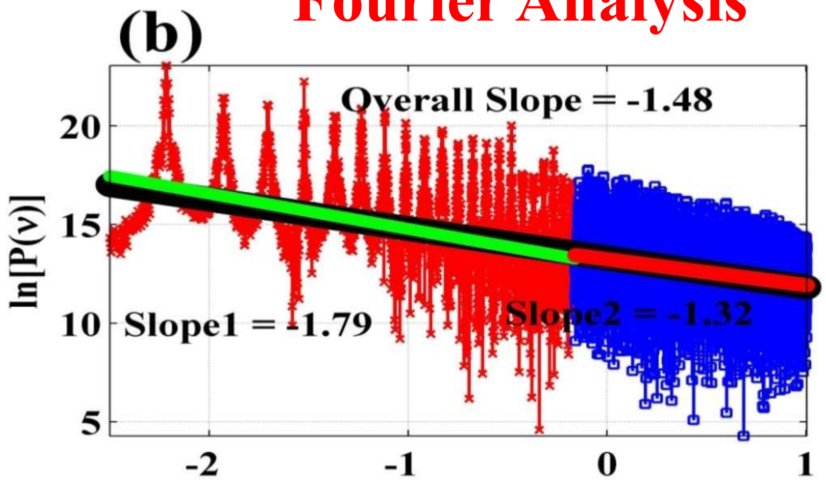
# Multifractal behavior in Spatial variation of refractive index

**Connective tissue of human uterine cervix** $n(\mathbf{r}) = \langle n(\mathbf{r}) \rangle + \delta n(\mathbf{r})$

**DIC Image**




**Fourier Analysis**

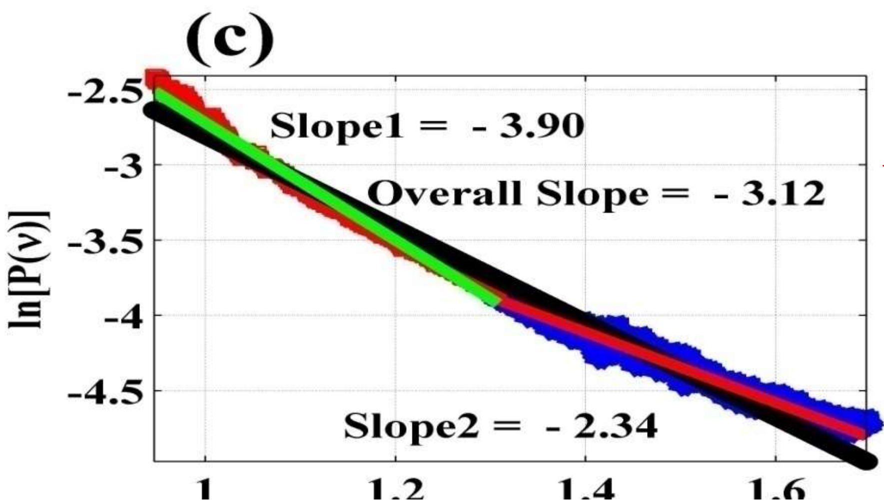



Multi-scale self-similarity in Spatial frequency (ν) distribution

**Slope: 2H+1**

**Hurst parameter 0 < H <1**

**Multiple Power law coefficients throughout ν range**



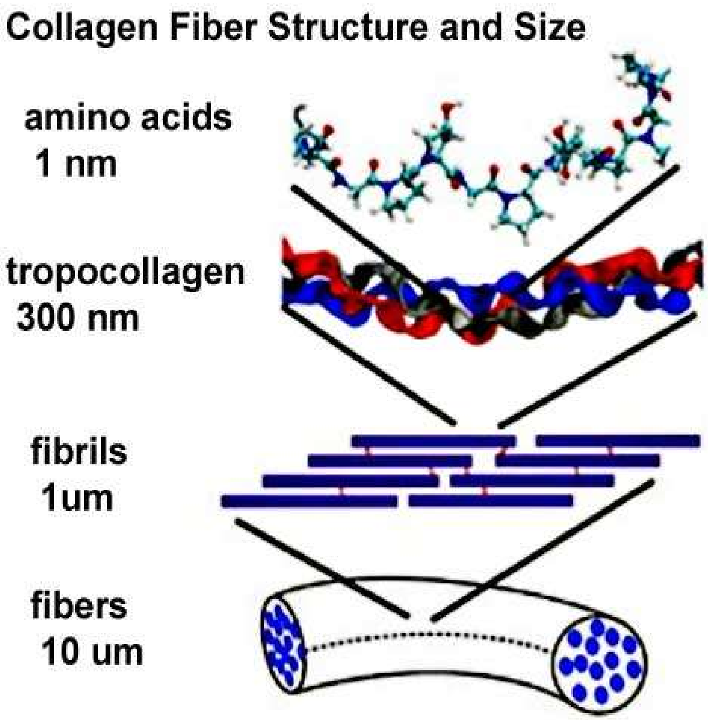

**Spatial frequency (ν) ↔ Wavelength variation of Scattering Intensity (Fourier)**

$$I\,(\nu);\; \nu = 2/\lambda \times \sin\left(\frac{\theta}{2}\right)$$ θ: **Scattering angle**

**Otherwise hidden Sub-diffractional information!!**

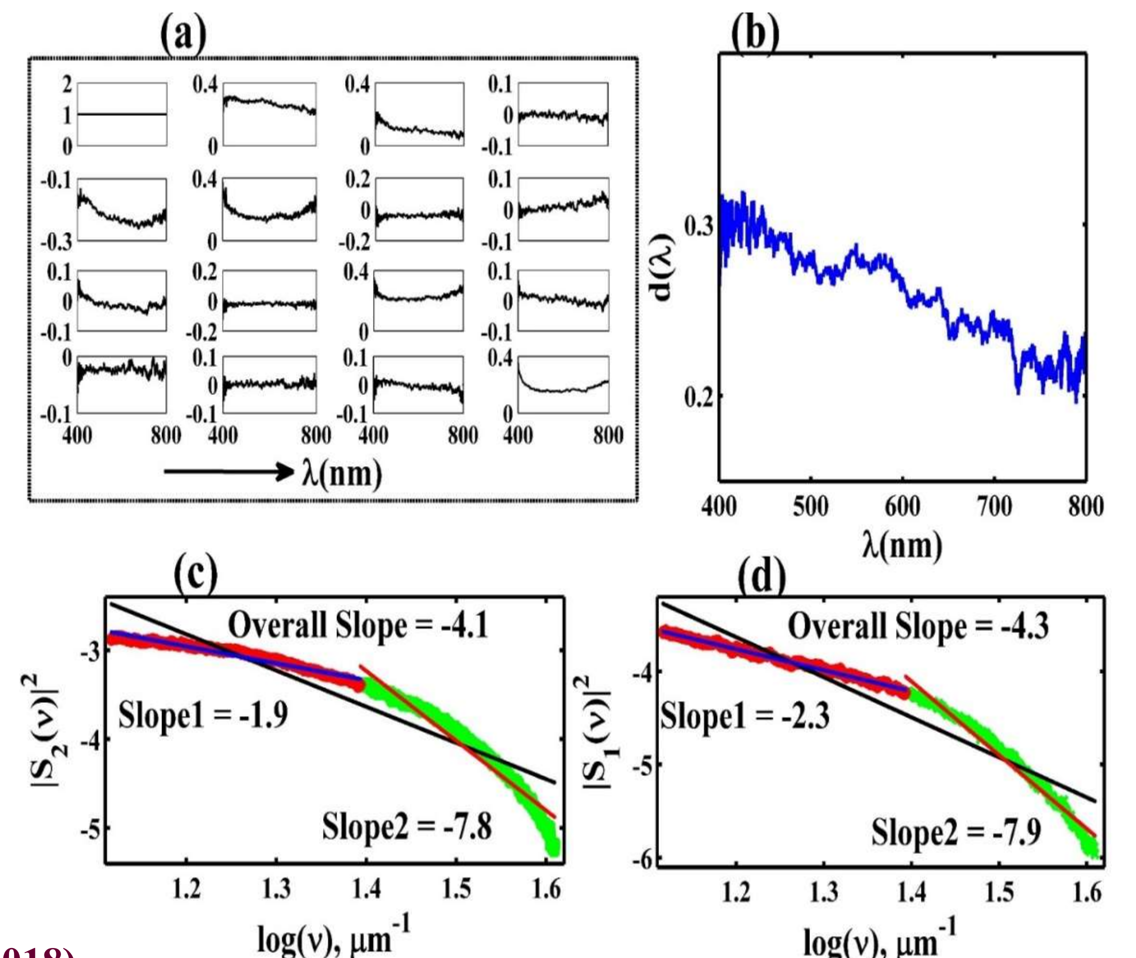
**J. Biomed. Opt., 21, 095004 (2016), Scientific Report, 4, 6129 (2014), Optics Letters, 38, 211 (2013)**

# Anisotropic Tissue structure & nano scale Multifractal anisotropy




**Self-similar fibrous network : Nano scale Multifractal anisotropy**

**Encoded in spectral Mueller matrix elements (Polarization resolved intensity)**




**Manifestations:**

**Different power law exponents for orthogonal Polarizations**

**Multiple power law exponents**

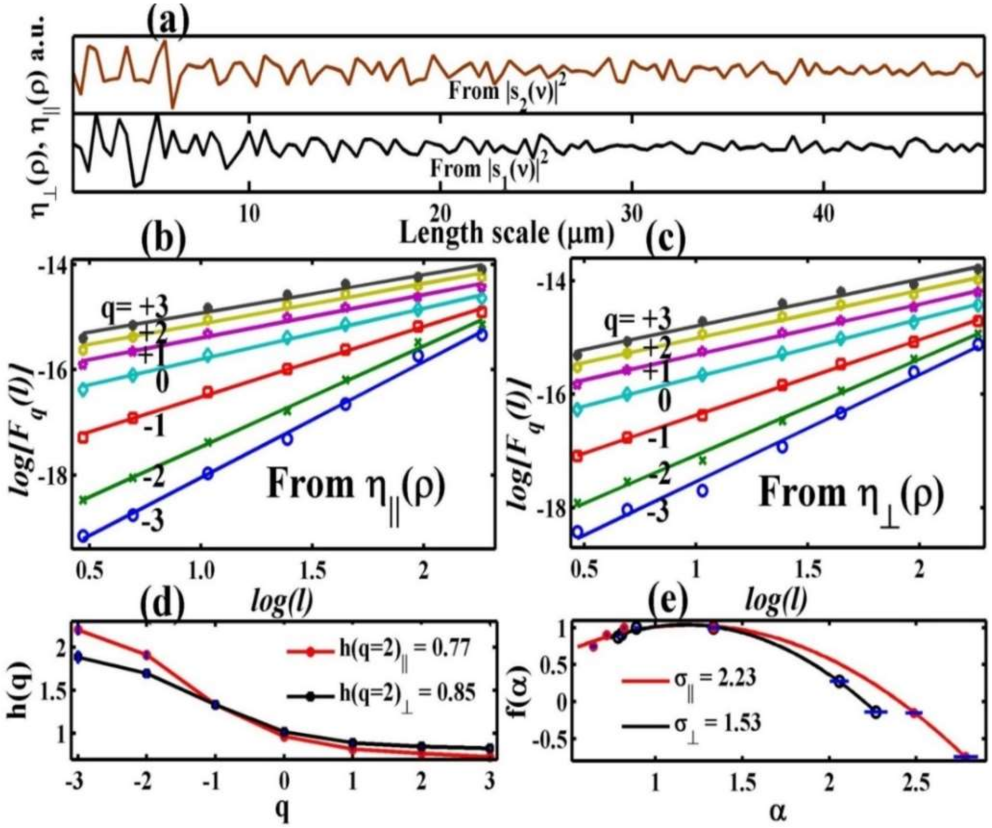
$$|s_{||}(\nu)|^2 \approx \nu^{-\gamma_{||}},$$

$$|s_{\perp}(\nu)|^2 \approx \nu^{-\gamma_{\perp}}$$

Optics Communications, 413 172–178 (2018)

# Extraction of Multifractal anisotropy

## Multifractal analysis on Fourier processed spectral Mueller matrix intensity elements

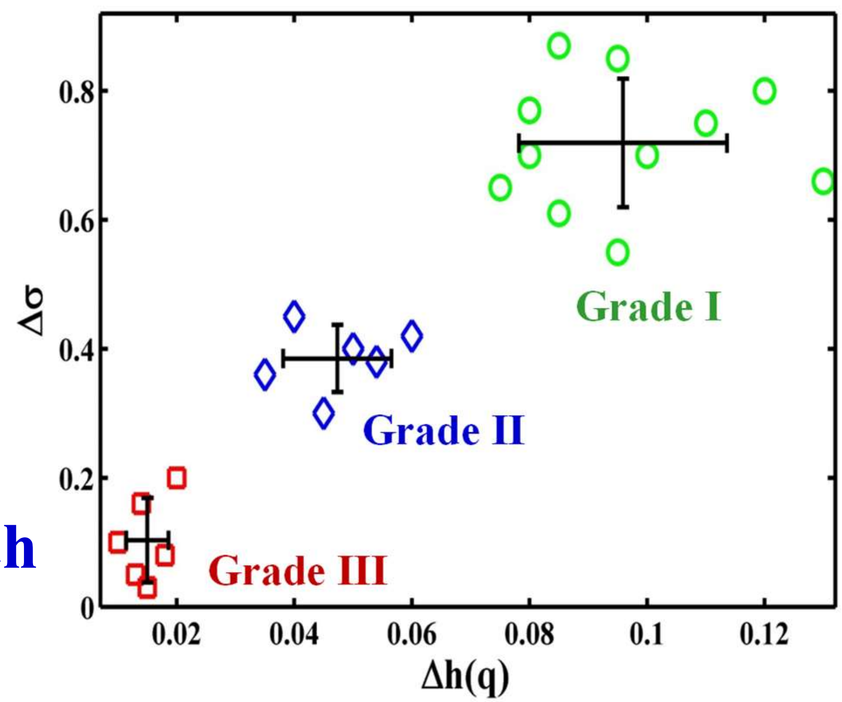



**$\sigma$: Width of singularity spectrum**

**Multifractal anisotropy**

$$\Delta\sigma = |\sigma_{||} - \sigma_\perp| = 0.70$$

$$\Delta h = |h(q=2)_{||} - h(q=2)_\perp| = 0.08$$




**Sub-diffractional (nano scale) anisotropic RI variations**

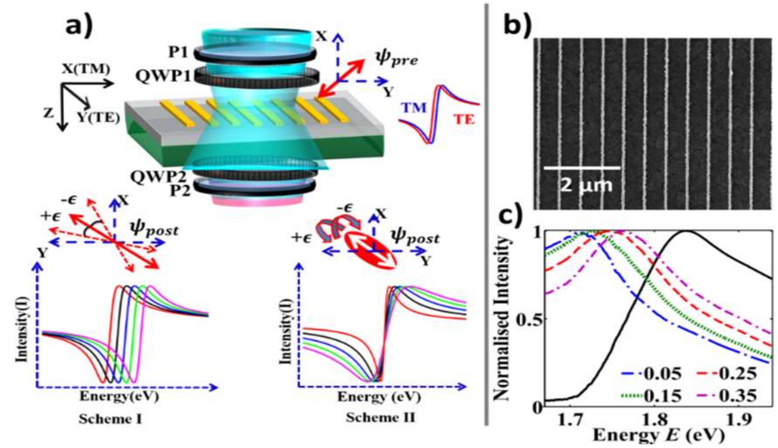
**Differences in multifractal anisotropy much pronounced than bulk anisotropy d & δ**

Laser Physics Letters, 15, 035601 (2018), Journal of Optics, 18, 125301 (2016)

# Polarimetry in Nano optics & Plasmonics

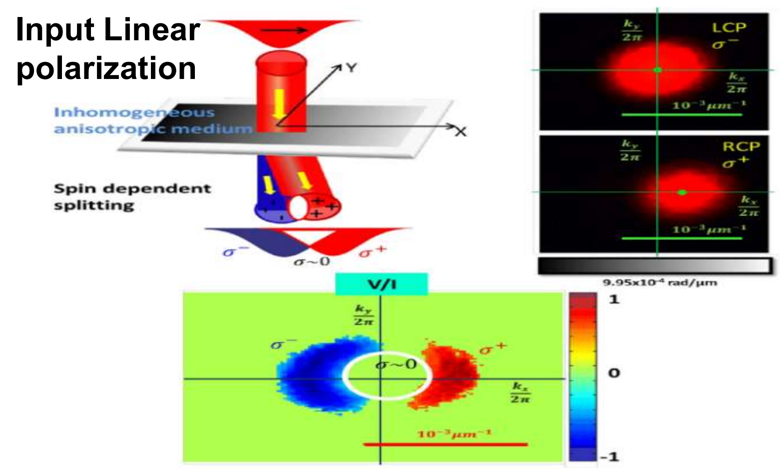
## Polarization controlled tuning of Fano resonance in plasmonic crystals

*ACS Nano*, 11, 1641, (2017), *Phys. Rev. A., 97, 053801 (2018),* Phys. Rev. A, 99, 032123 (2019)
Optics Express, 24, 6041 (2016)

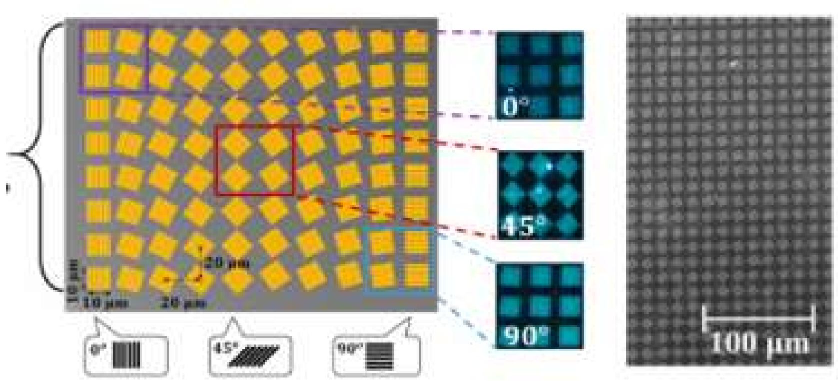



## Spin orbit interaction of light in plasmonic metamaterials

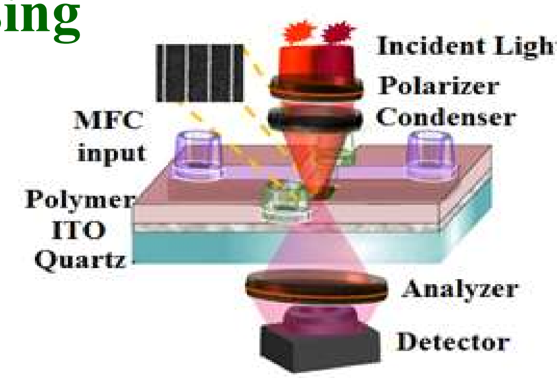
*Phys Rev. A, 2022,* Communications Physics, 4, 102 (2021), *JOSA B., 38, 2180 (2021), Phys. Rev. A*, 102, 033518 (2020), Scientific Reports, 10, 11464 (2020), *Phys. Rev. A*, 100, 033805 (2019), Phys. Rev. A., 97, 043823 (2018), Optics Letters, 41, 4499-4502 (2016), Scientific Reports, 6, 39582 (2016)




## Geometric phase meta-surface - manipulation of light at nanometer scale




## Plamonic crystal metadevice for Arsenic sensing



**THANK YOU**