Terahertz Time Domain Spectroscopy of Gold Nanorod/Polymer Films

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Nanoparticles have distinct electrical and vibrational properties from bulk materials originating from the quantum confinement and surface effect. Bioengineers are currently able to exploit these properties for applications in biosensing, using the surface plasmon resonance wavelength of gold nanorods to monitor changes in their local environment. THz-TDS provides scientists with new opportunities to study low frequency phonons, and low frequency phonons in gold nanoparticles are explicatory of their morphology. Here, terahertz time-domain spectroscopy (THz-TDS) was used to study the vibrational behavior of gold nanorods embedded in a poly(vinyl alcohol) matrix. The nanorods' aspect ratios (diameter x length) of 30.7 x 81.6 nm, 30.7 x 84.0 nm, 16.2 x 39.5 nm, 18.7 x 52.2 nm, and 18.5 x 56.5 nm are confirmed by visible/near-infrared absorption spectroscopy and transmission electron microscopy. The frequencies of the phonon modes are expected to be proportional to the longitudinal and transverse sound velocity in the material and inversely proportional to the size of the Au nanorods. We discuss how THz-TDS offers a solid method to determine nanoparticle morphology.

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Purpose

- Vibrational phonon modes in gold nanorods are fingerprints of their shape and size[1]
- Tuning the aspect ratios of gold nanorods can change the frequencies at which phonon modes are observed

Methods

Transmission electron microscopy (TEM):

- Forms an image by passing electrons through the sample
- Allows us to accurately measure nanoparticle dimensions

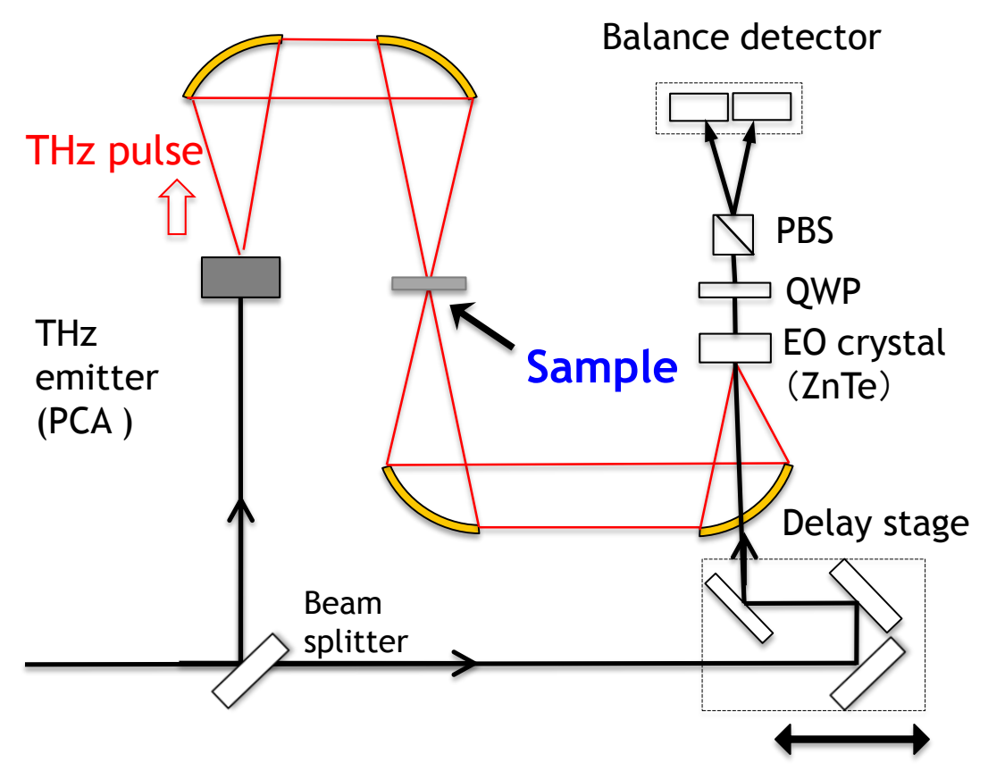
Visible-near infrared absorption:

- Measures the absorption of a sample as a function of wavelength
- Allows us to determine peak plasmonic absorption wavelengths

Terahertz time domain spectroscopy (THz-TDS)

- Measures the THz electric field strength as a function of time
- With fast fourier transforming, we are able to determine phonon vibrational modes absorption frequencies

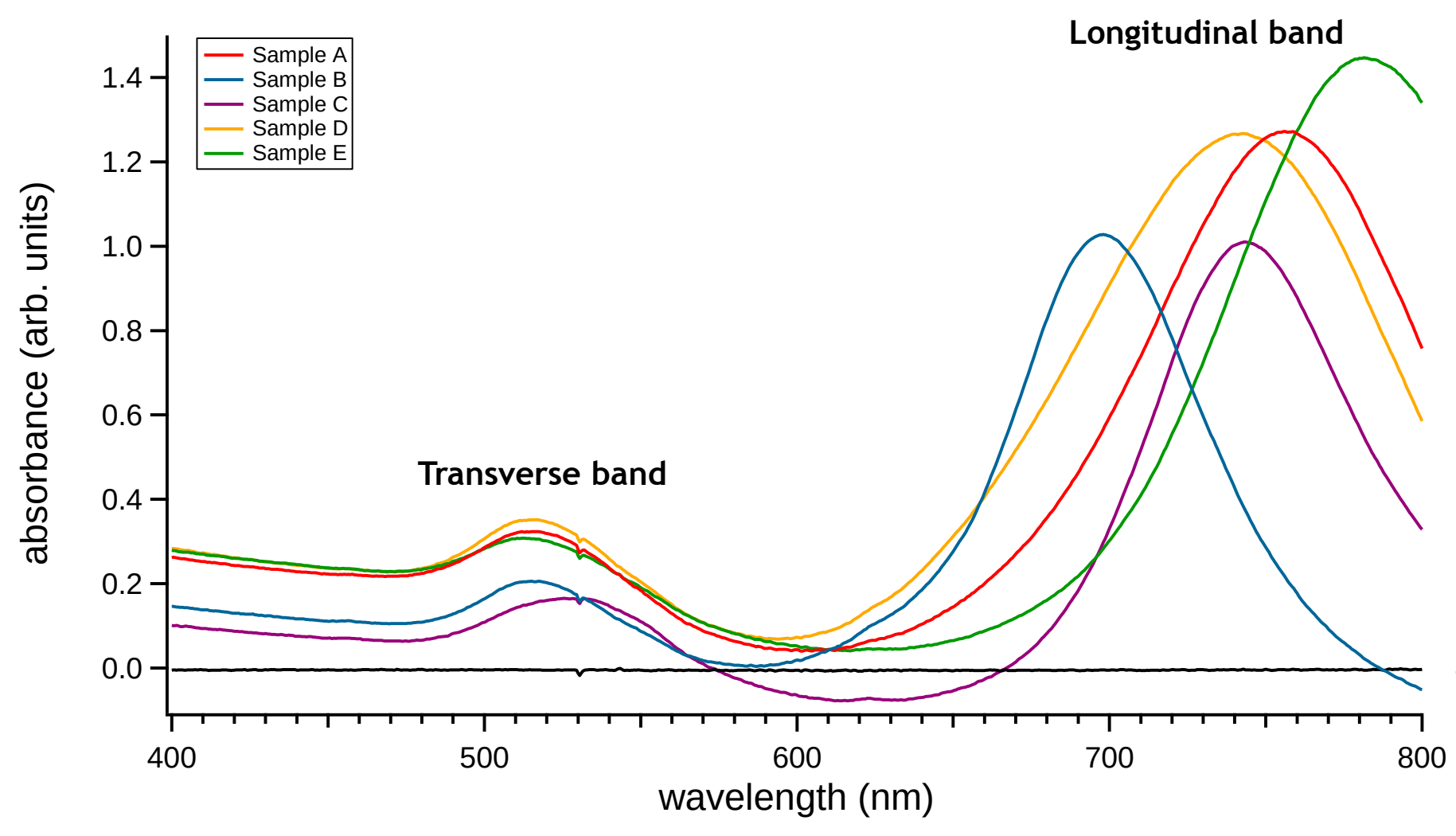
Experimental THz-TDS set up:



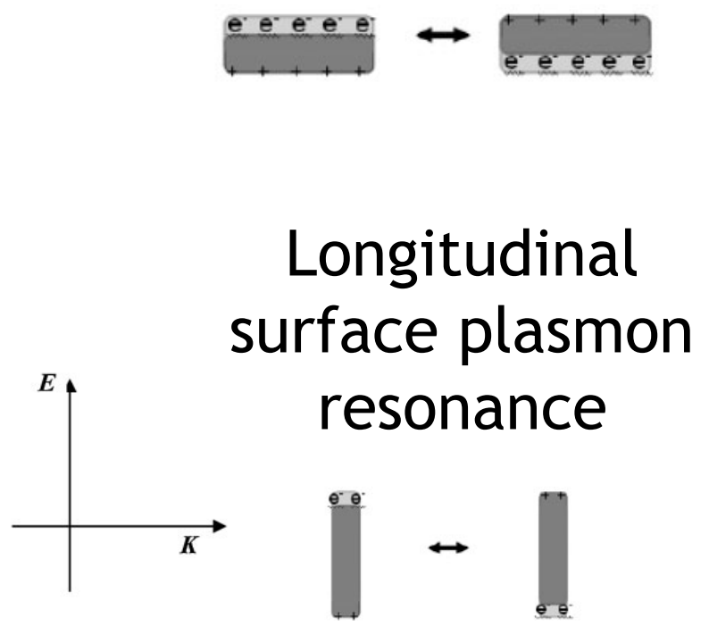
PCA: photoconductive antenna
PBS: polarizing beam splitter
QWP: quarter wave plate

Results

Visible-near infrared absorption spectra:



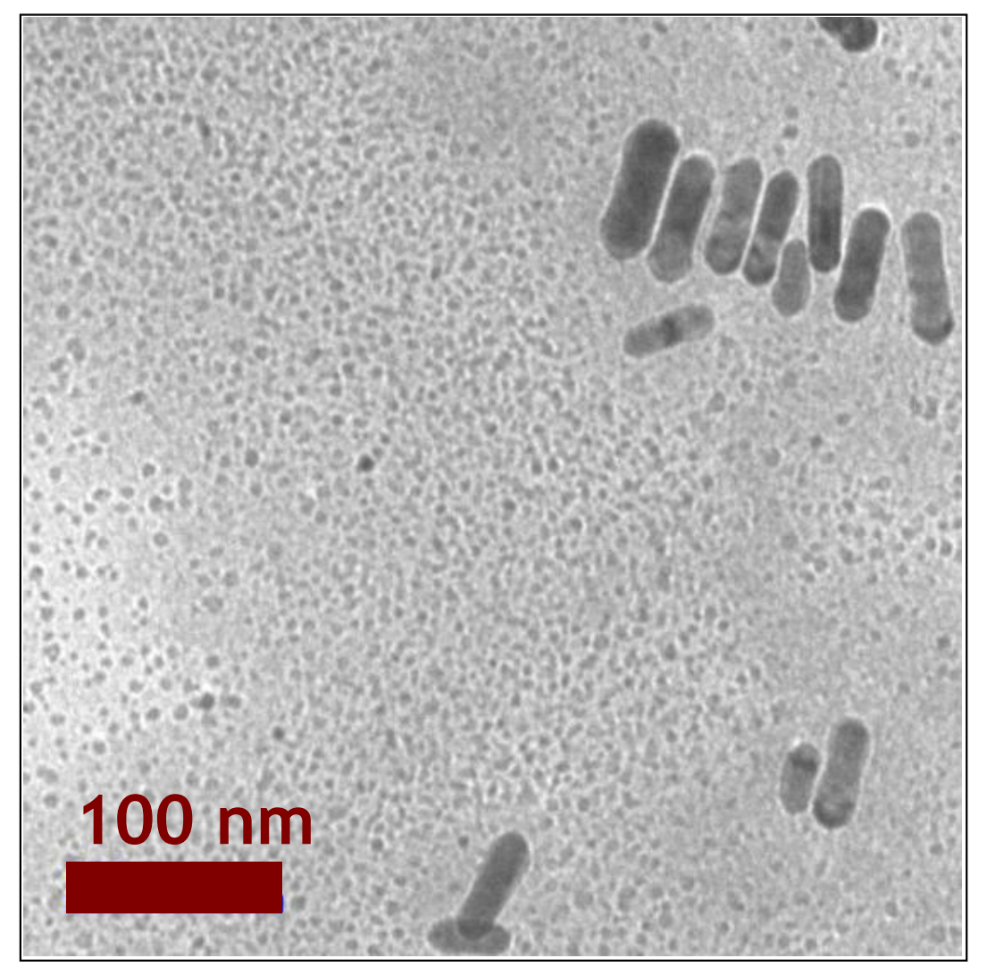
Transverse surface plasmon resonance



Longitudinal surface plasmon resonance

Results

TEM image:

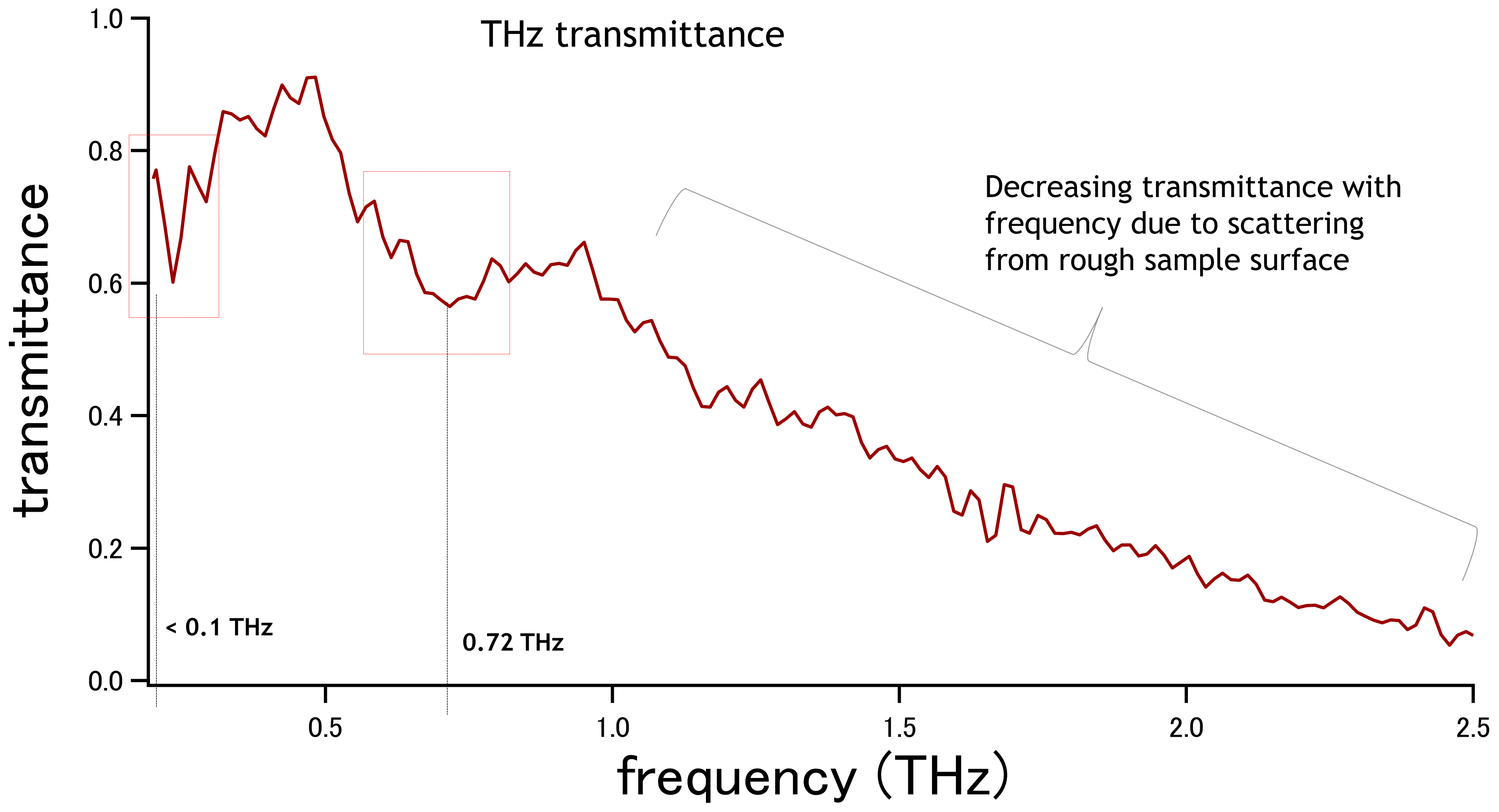


Sample E

Aspect ratios and plasmon resonance wavelengths:

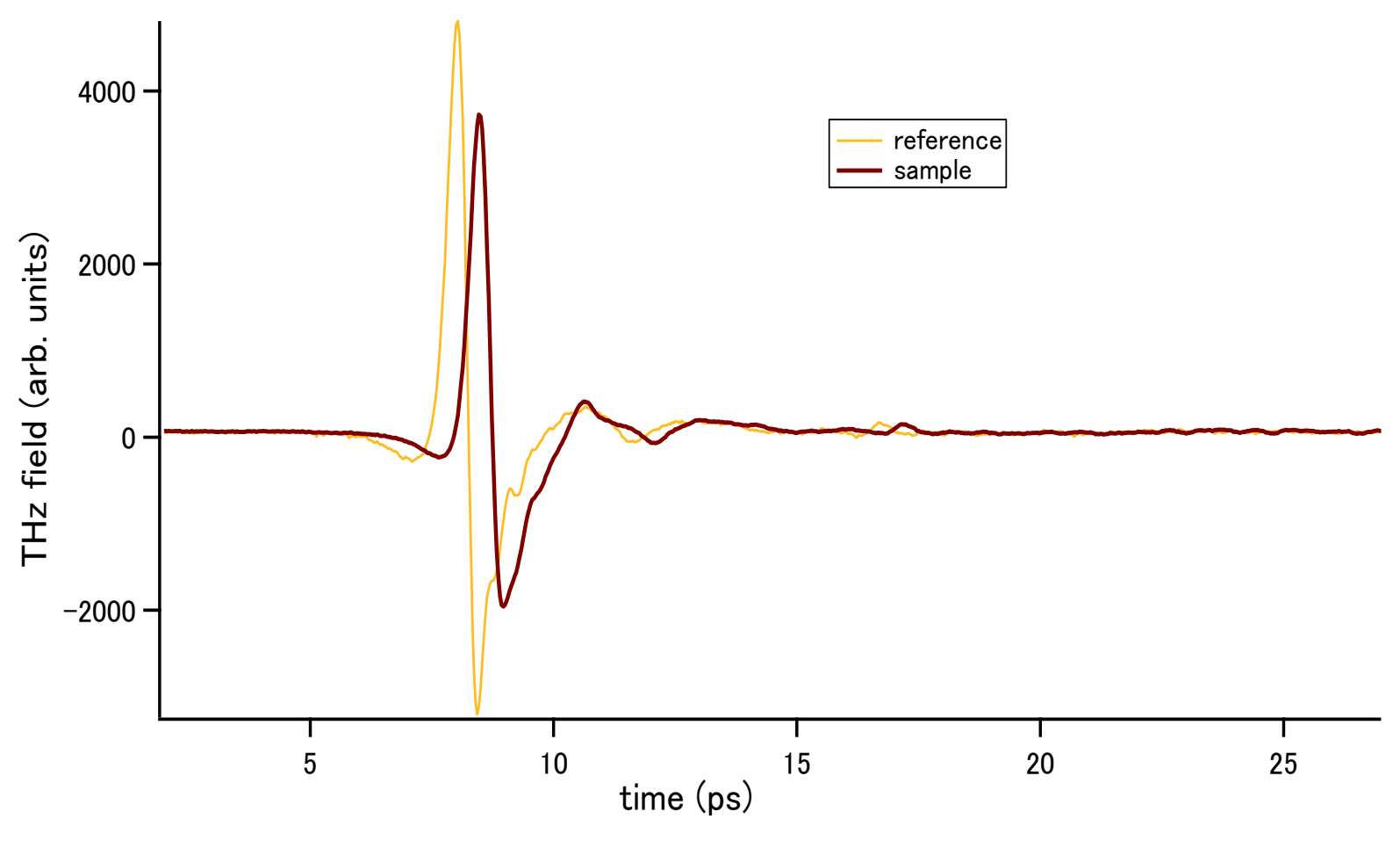
sample	average length (nm)	average diameter (nm)	average aspect ratio (length/diameter)	longitudinal resonance wavelength (nm)	transverse resonance wavelength (nm)
A	81.58	30.7	2.66	756	516.25
B	84	30.67	2.74	698	516.25
C	39.47	16.23	2.43	743.5	525
D	52.24	18.69	2.95	740	516
E	56.46	18.51	2.93	780	512.25

THz-TDS with sample E (in PVA polymer matrix):

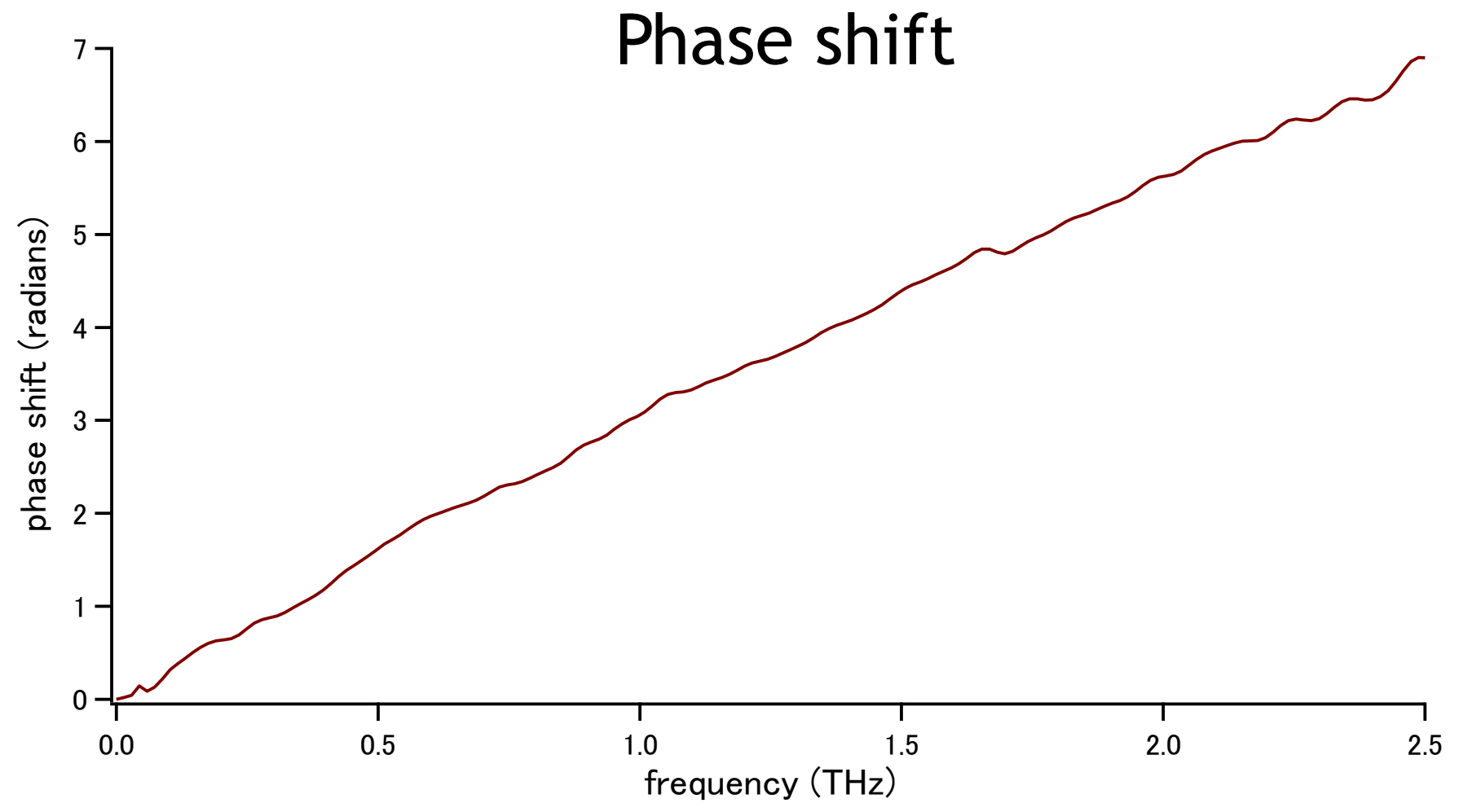


Decreasing transmittance with frequency due to scattering from rough sample surface

THz time trace



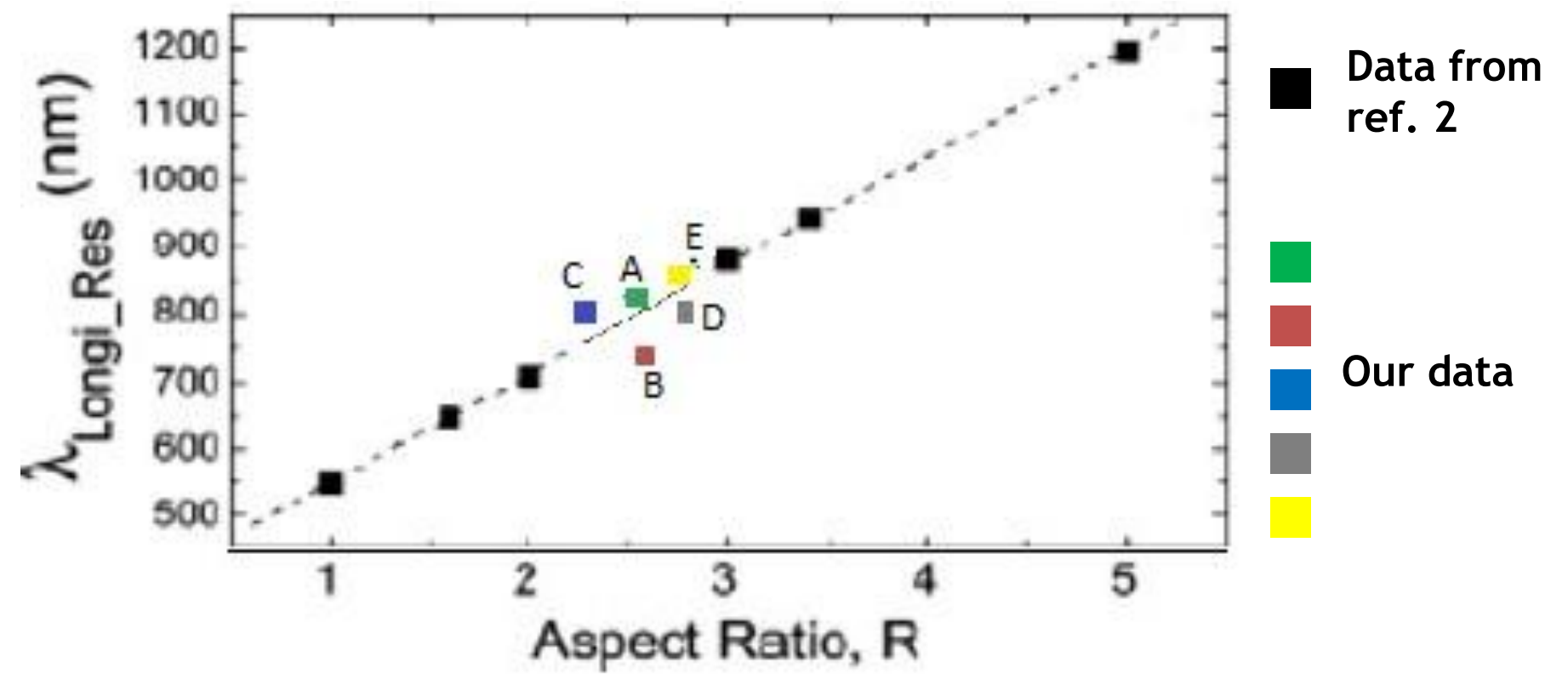
Phase shift



Analysis

Plasmonic resonance wavelengths:

- Data closely follows trends shown by previous studies



Origin of the THz transmittance dip:

For 2.5 aspect ratio [4]

$$\omega_{ext} = \frac{2n+1}{L}\pi\sqrt{\frac{E}{\rho}}$$

L = 56.46 nm
ρ = 19.3 g/mL
E = 79 GPa
n = 0

$$f_{ext} = \frac{\omega_{ext}}{2\pi} = 0.0179\,THz$$

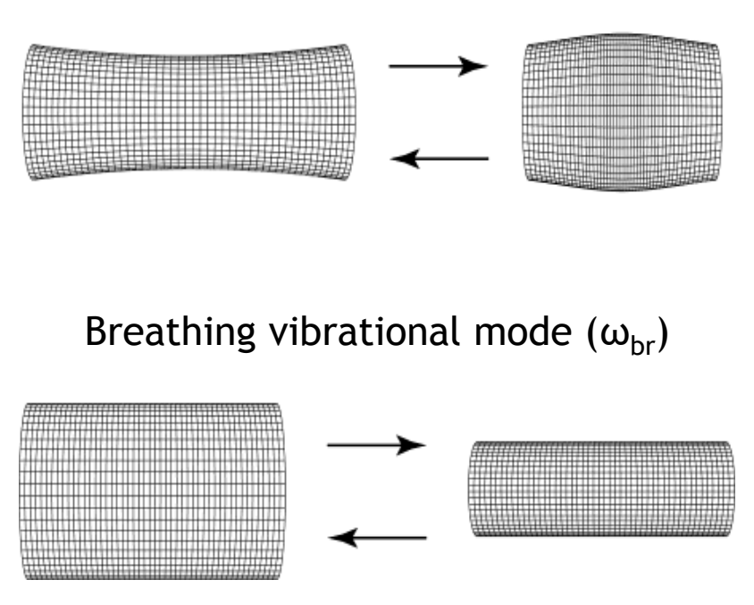
$$\omega_{br} = \frac{\tau_n}{a}\sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}}$$

ρ = 19.3 g/mL
E = 79 GPa
ν = 0.42
$\frac{\tau_n}{a}$ = constant (n = 0, fundamental mode)

$$f_{br} = \frac{\omega_{br}}{2\pi} = 0.1075\,THz$$

Extensional vibrational mode (ω_{ext})

Breathing vibrational mode (ω_{br})



- Possible low frequency phonon absorption near 0.10 THz due to fundamental breathing mode
- Higher order breathing mode absorption near 0.72 THz

Conclusions

- Ultraviolet-visible spectrophotometry works to determine the peak plasmonic absorption wavelengths found for gold nanorods
- TEM imaging is a reliable method to determine the aspect ratios of gold nanorods in solution
- THz-TDS was used to detect slight phonon absorption (breathing vibrational mode) in gold nanorods

References

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