

*Understanding
the UV-visible-NIR scattering
of non-spherical
metallic nanoparticles*



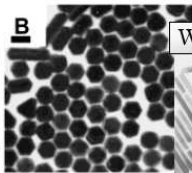
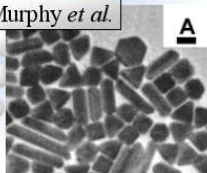
Stuart W. Prescott, Paul Mulvaney

Particulate Fluids Processing Centre
School of Chemistry
University of Melbourne

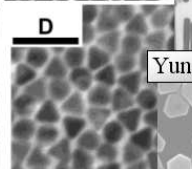
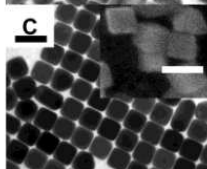
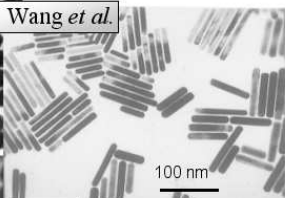


Recent synthetic achievements

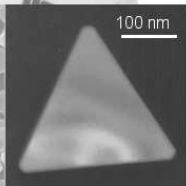
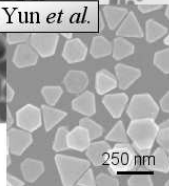
Murphy *et al.*



Wang *et al.*



Yun *et al.*



scale bars = 100 nm



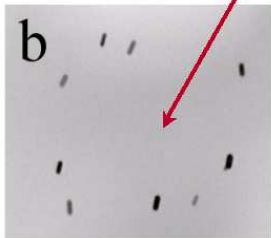
Uses of nanorods

Au nanorods (AR ~ 2.9) in a PVA film

randomly oriented



after PVA stretched



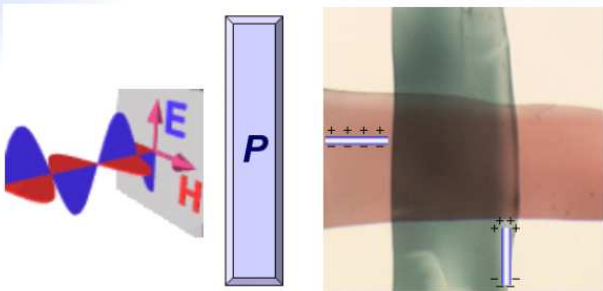
Pérez-Juste *et al.* *Advanced Functional Materials*, 15, 1065, 2005

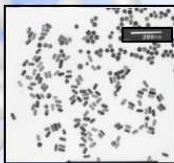


Uses of nanorods

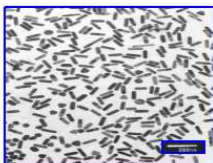
Stretching of PVA aligns rods

- photograph under polarised light:





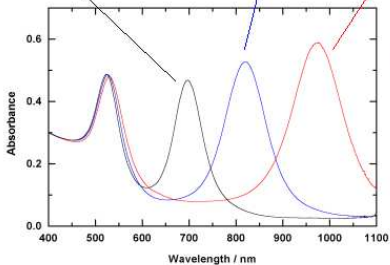
A.R.: 2.25
Width: 20.7 nm
Length: 46 nm



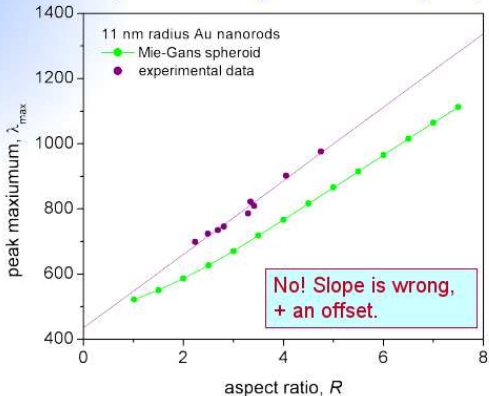
A.R.: 3.35
Width: 22.4 nm
Length: 75 nm



A.R.: 4.75
Width: 22.8 nm
Length: 108 nm



Are these prolate spheroids (ellipsoids)?

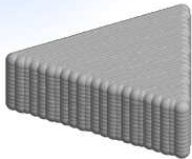


All spectra are for gold nanorods in water



Correctly predicting λ_{\max}

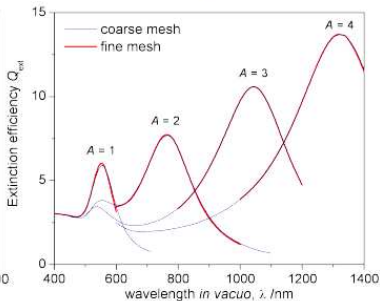
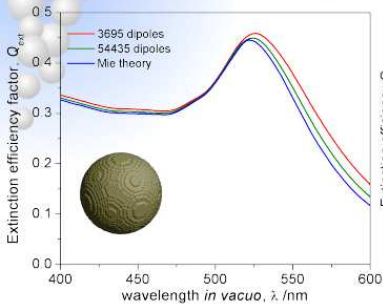
Investigating influence of
particle shape and size:



Discrete Dipole Approx. Model
Cubic array of dipoles (Draine & Flatau)



Checking DDA for nanoparticles



DDA captures
target and
spectrum features

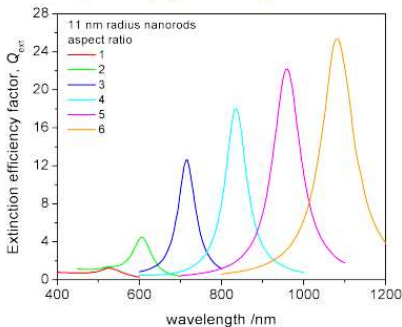
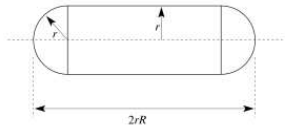


34189 dipoles
294293 dipoles

DDA for Au spherically capped cylinders

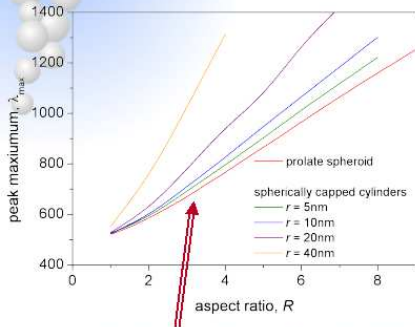
For aspect ratio, R

- spherical end cap, radius r
- particle length $2rR$
- cylinder length $2r(R-1)$



λ_{max} varies with R , and becomes more intense

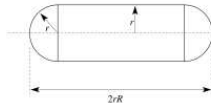
λ_{\max} varies with rod width?



prolate spheroid, $R = a/b$



spherically capped cylinder



λ_{\max} independent of rod width
for Mie-Gans prolate spheroid

Also recently reported by Brioude, *et al.*,
J. Phys. Chem. B, 109, 13138, 2005.



Spectra & Geometrical Factors

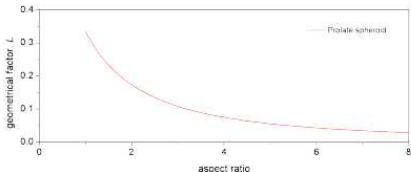
Polarisability, α , gives extinction:

- single parameter expression for $Q_{\text{ext}}(\lambda)$
- geometrical factor L (sphere has $L=1/3$)

$$\alpha = V \frac{\epsilon - \epsilon_m}{\epsilon_m + L(\epsilon - \epsilon_m)}$$

$$Q_{\text{ext}}(\lambda) = \frac{2\pi\sqrt{\epsilon_m}}{G\lambda} \text{Im}\{\alpha\}$$

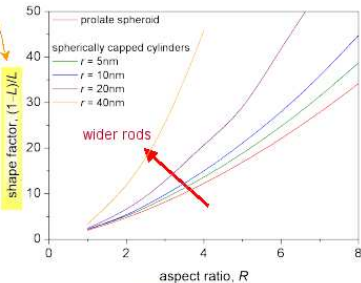
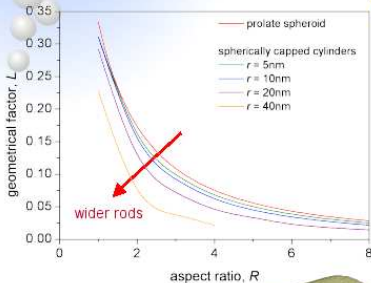
$$Q_{\text{ext}}(\lambda) = \frac{2\pi V \epsilon_m^{3/2}}{GL^2\lambda} \frac{\epsilon''}{\left(\epsilon' + \frac{1-L}{L}\epsilon_m\right)^2 + (\epsilon'')^2}$$



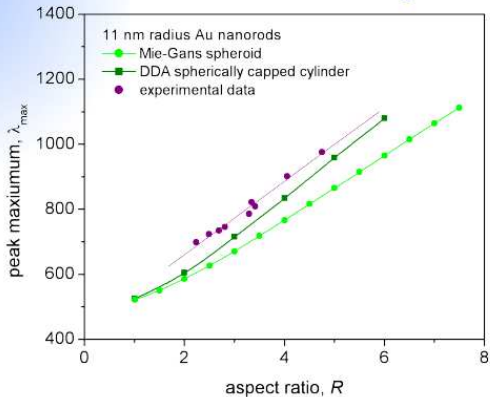
(L shown for longitudinal mode only)

$$Q_{\text{ext}}(\lambda) = \frac{2\pi V \varepsilon_m^{3/2}}{GL^2 \lambda} \frac{\varepsilon''}{\left(\varepsilon' + \frac{1-L}{L} \varepsilon_m\right)^2 + (\varepsilon'')^2}$$

L and rod width



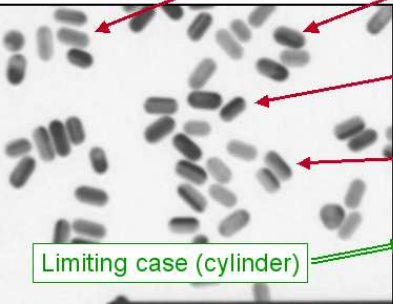
DDA gets closer...



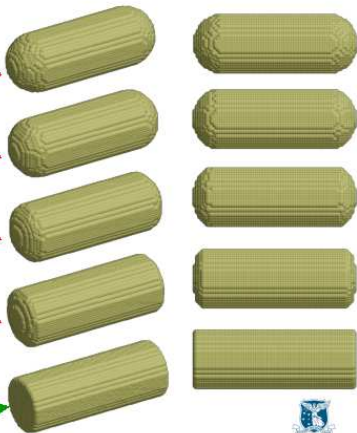
... but there is room for improvement

End-cap effects

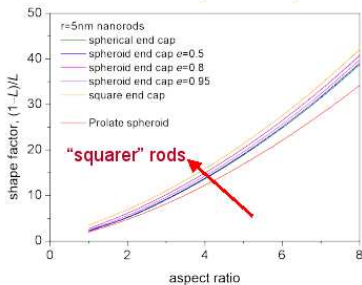
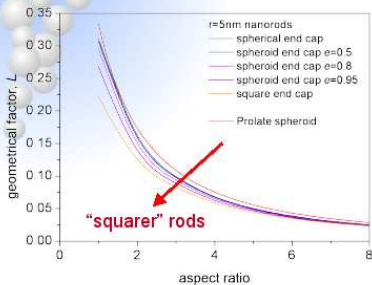
Does end-cap geometry change spectrum?



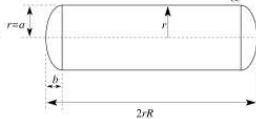
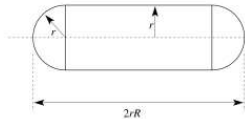
Limiting case (cylinder)



L and end-cap shape

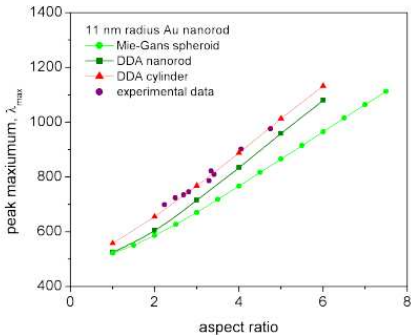
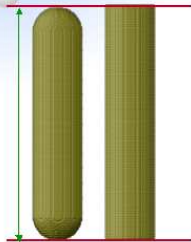


For the spheroid end caps, eccentricity: $e^2 = 1 - \frac{b^2}{a^2}$



Limits on λ_{\max} using DDA

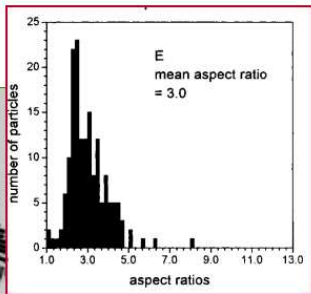
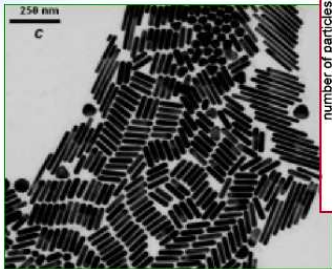
λ_{\max} should be between cylinder and rod:



... cylinders seem to be the closest geometry?
something must be wrong...

Sample purity

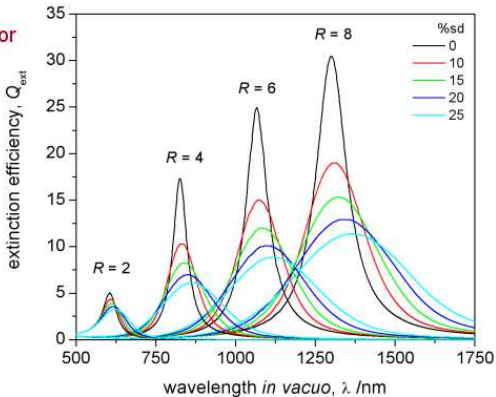
How does a distribution of rods sizes change the spectrum?



Example data from Yu *et al.*, *J. Phys. Chem. B*, 101, 6661, 1997.

"Synthetic" spectra

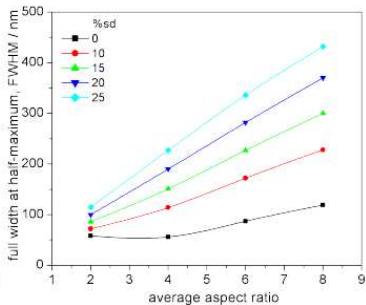
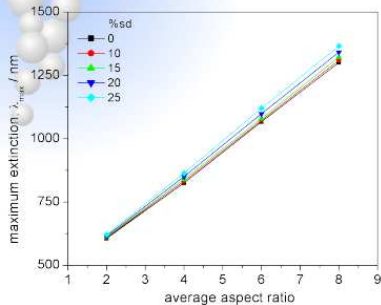
1. Find functional form for geometrical factor, $L(R, r)$
2. Calculate spectra for each bin in discrete particle length distribution
3. Add weighted component spectra



Geometrical factor, L , becomes powerful tool



Limits from “synthetic” spectra



- red-shift of λ_{\max} due to broadening of distribution
- FWHM also increases

Conclusions: predicting λ_{\max}

Must consider:

- particle shape
 - these are nanorods *not* ellipsoids
 - width is important *not just aspect ratio*
- subtle end effects
 - spheroid end cap?
- particle size distribution
 - control it? reduce it? purify?



Conclusions: characterisation

Spectrometric characterisation of nanorods...

- for a given aspect ratio,
 - ellipsoid model gives uniquely determined λ_{\max}
 - DDA: λ_{\max} depends on width too
- with an independent measure of width...
 - ...and known end-cap geometry...
 - ...and a Gaussian distribution
 - (λ_{\max} , FWHM) uniquely determines
 - ❖ “light-scattering average” aspect ratio
 - ❖ standard deviation of distribution



Acknowledgements

- Support of the Victorian Institute for Chemical Sciences High Performance Computing Facility is gratefully acknowledged.
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Copies available from nanonano.net

