Nanoprobe enhanced optical spectroscopy

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Optical microscopy

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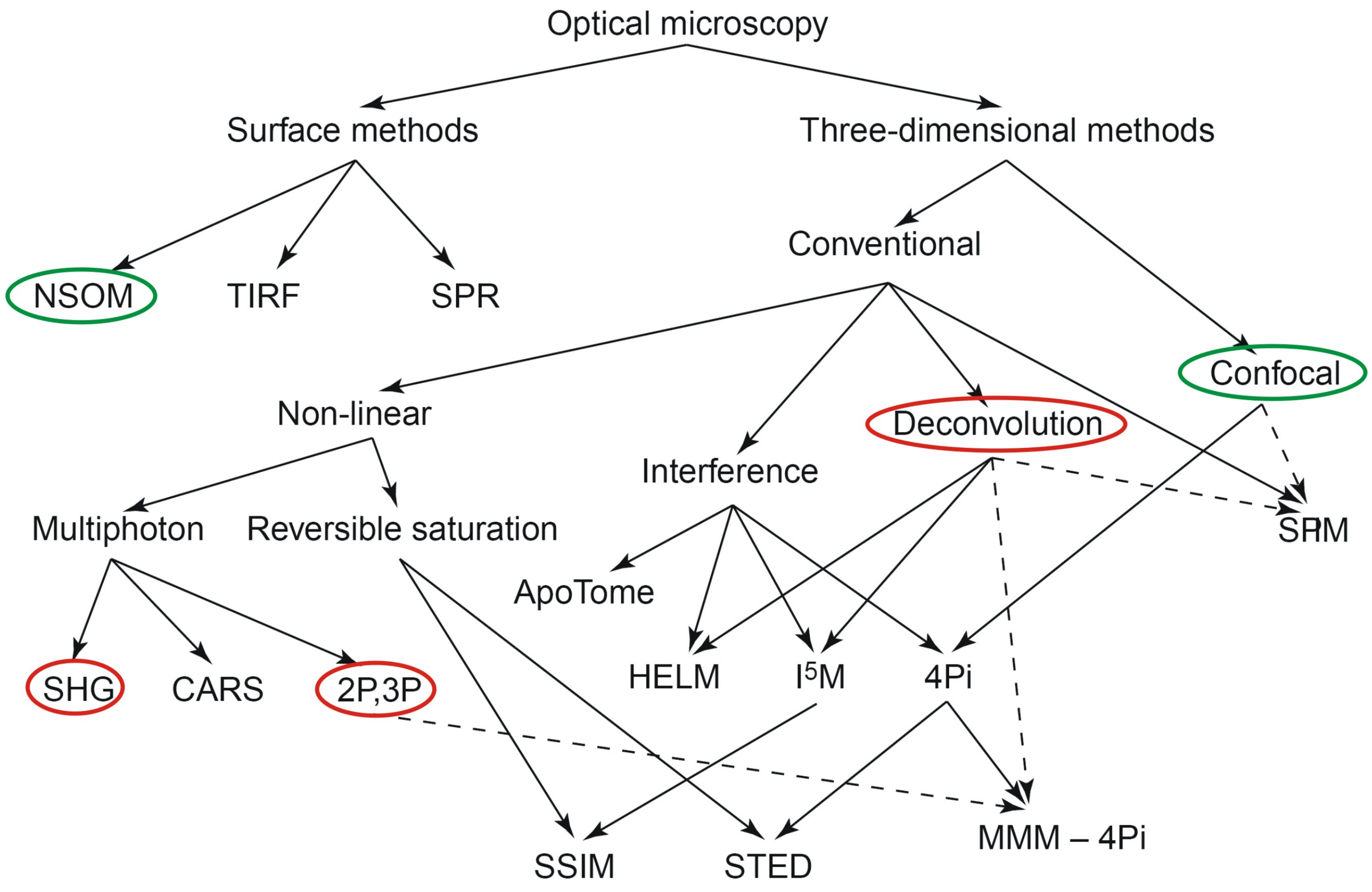
- Rayleigh criteria:
  - $d_{x,y} = 0.61\lambda/NA$
  - $d_z = 2\lambda/NA^2$



Y. Garini et al., Curr. Opin. Biotech. ***16****, 1 (2005).*

Comparison of optical microscopes

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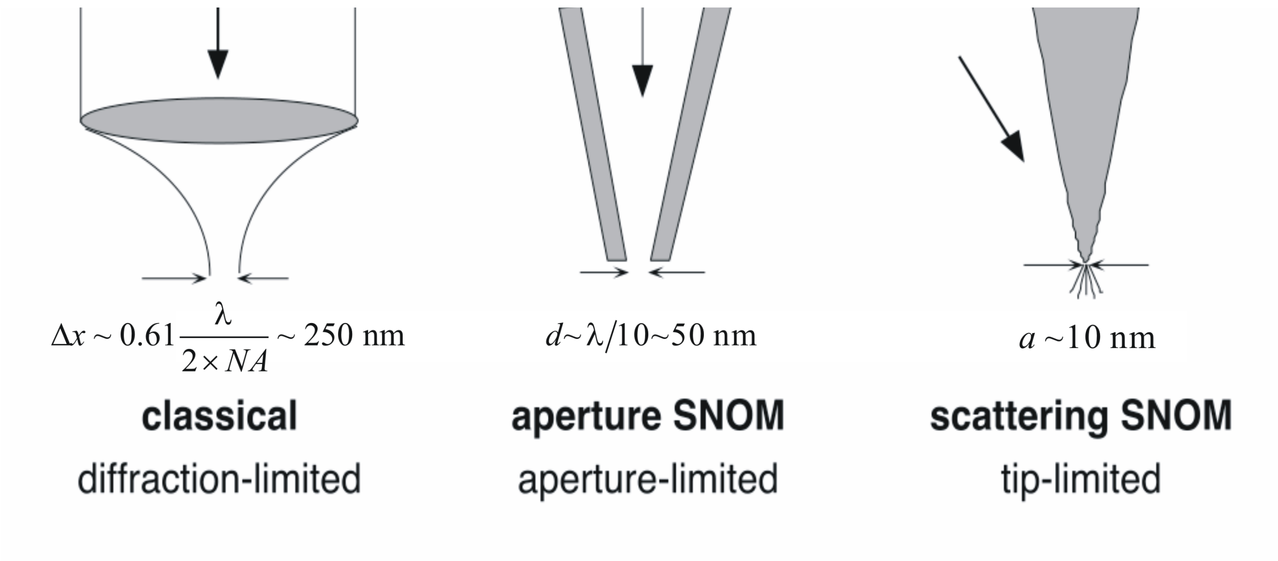
- Performing optical spectroscopy in nanometer scales is one of the critical steps in the development of nanoscience and nanotechnology.
- Two key issues in characterization in nanometer scales:
  - Nanometer-scaled resolution
  - Signal amplification
- New physics involving light-matter interaction in nanometer scales need to be developed.



Limits of aperture-type SNOM

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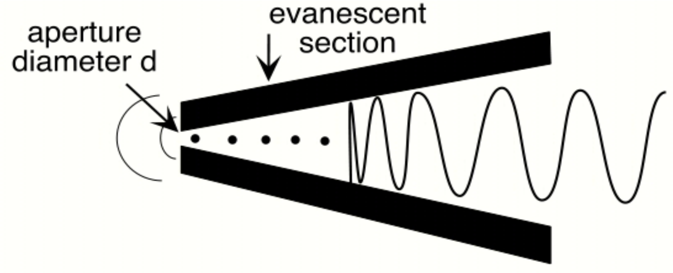
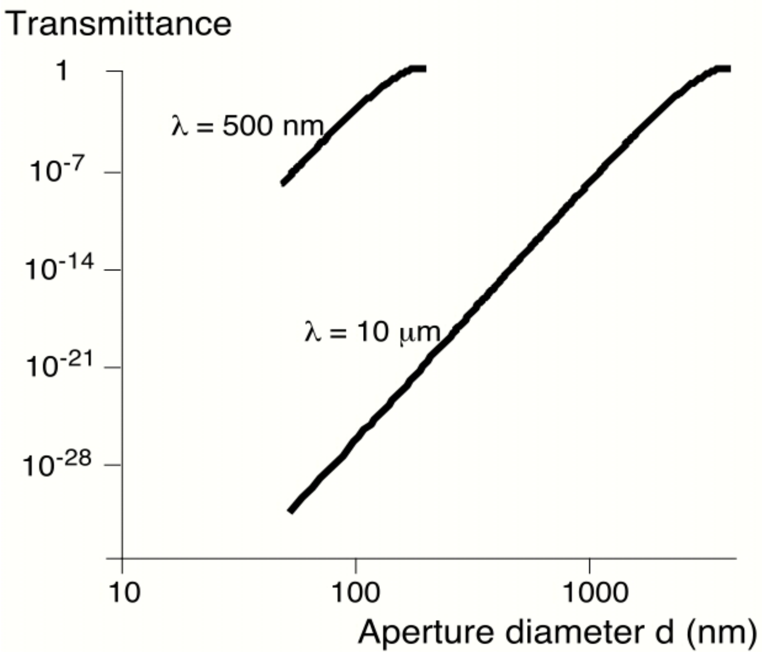
- Low optical throughput
- Spatial resolution: >50 nm
- Wavelength dependent throughput





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Nanoprobe enhanced optical microscopy

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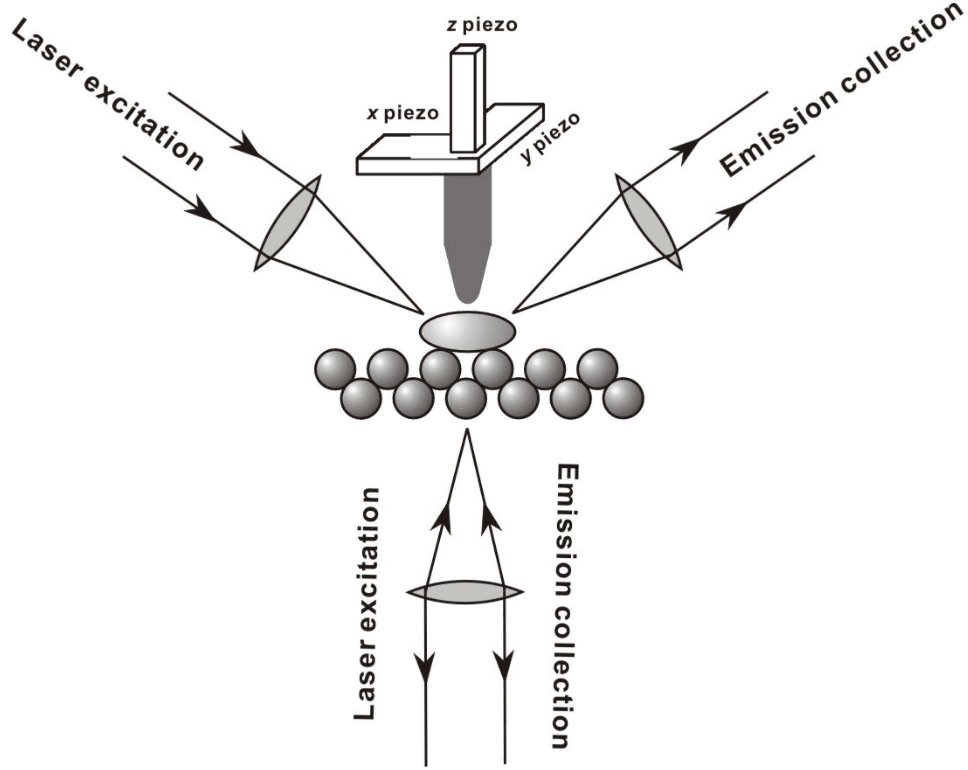
- **Scattering-SNOM**
  - collecting elastic scattering signal
- **Tip-enhanced spectroscopy**
  - collecting inelastic scattering signal (Raman or fluorescence)
- **Nanostructure-enhanced spectroscopy**



Lycurgus Cup in Roman times

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The glass appears green in daylight (reflected light), but red when the light is transmitted from the inside of the vessel.

The Lycurgus Cup, Roman (4th century AD), British Museum
F. E. Wagner et al., Nature 407, 691 (2000).

Mysterious red color in Lycurgus Cup

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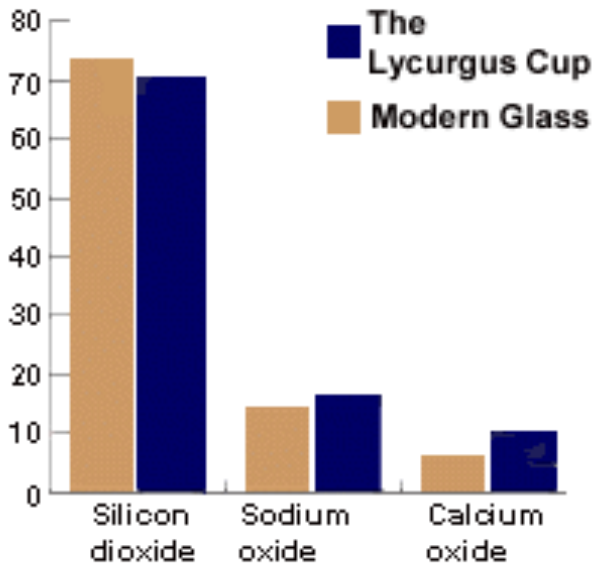
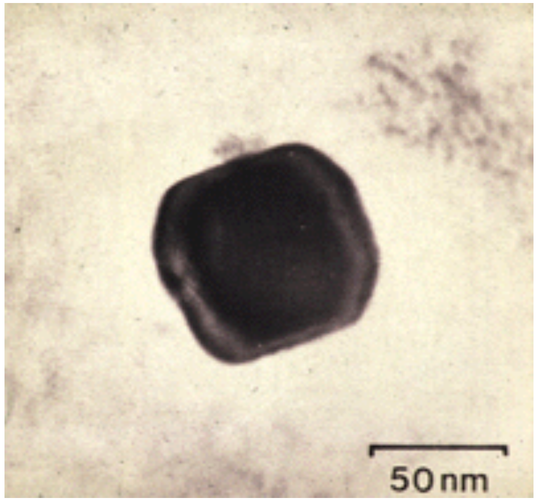


The same composition as modern glass



X-ray analysis:
70% Ag + 30% Au

These Ag-Au nanoparticles (~300 ppm) scatter the light, rather in the same way that fine particles in the atmosphere cause a 'red sky at night' effect. They cause the color effects shown by the Cup.

The Lycurgus Cup, Roman (4th century AD), British Museum (www.thebritishmuseum.ac.uk)

Scattering by a metal sphere

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Induced dipole by the applied field

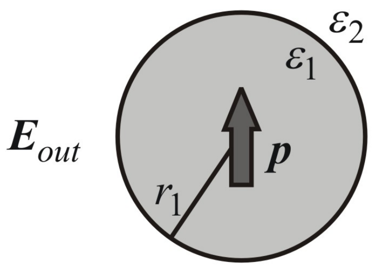
$$\boldsymbol{E}_{out} = E_0 \boldsymbol{e}_z + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{r_1^3}{r^3} E_0 \left(2\cos\theta \boldsymbol{e}_r + \sin\theta \boldsymbol{e}_\theta \right)$$

$$\Downarrow$$

$$\boldsymbol{p} = \varepsilon_2 \alpha E_0$$

Effective dipole inside the sphere

$$\alpha = 4\pi r_1^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}$$



Near-field radiation power from $\boldsymbol{p}(t)$ (near-field scattering cross section)

$$C_{sca}(r) = \int_0^{2\pi} d\theta \int_0^{\pi} d\phi \left| \boldsymbol{E} \right|^2 r^2 \sin\theta = \frac{\alpha^2}{6\pi} \left(\frac{3}{r^4} + \frac{k^2}{r^2} + k^4 \right)$$

$\boldsymbol{E}$: the near-field electric field by $\boldsymbol{p}(t)$

$$C_{sca}^{NF} = C_{sca}(r) = \frac{\alpha^2}{6\pi} \left(\frac{3}{r_1^4} + \frac{k^2}{r_1^2} + k^4 \right)$$

G. Mie, Ann. Phys. (N.Y.) ***25****, 377 (1908).*

Electron collective motion in metal clusters

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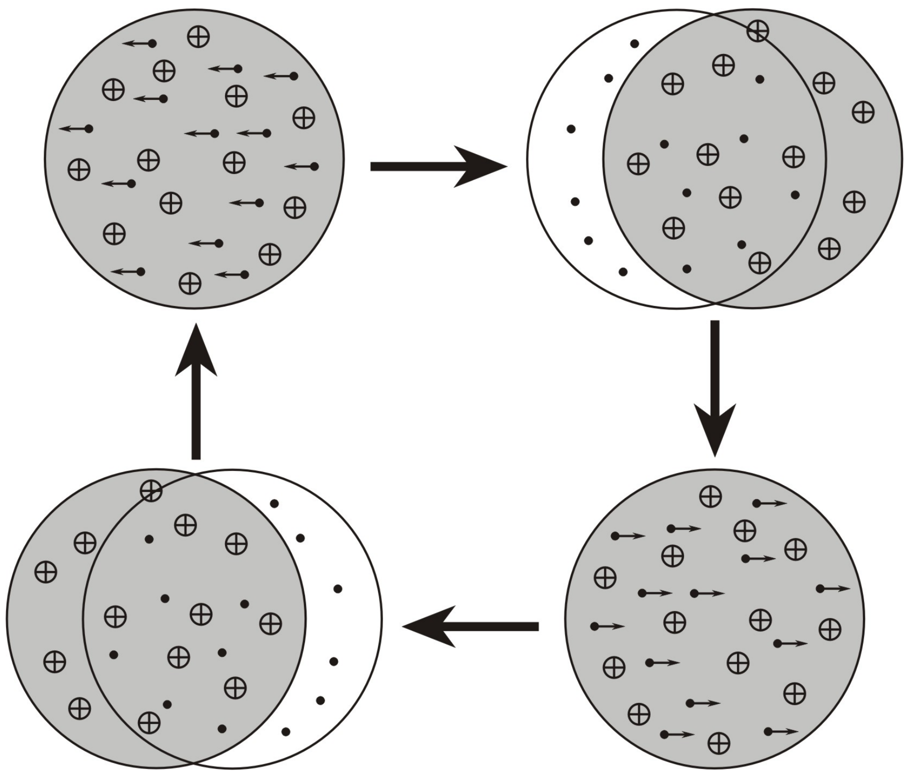
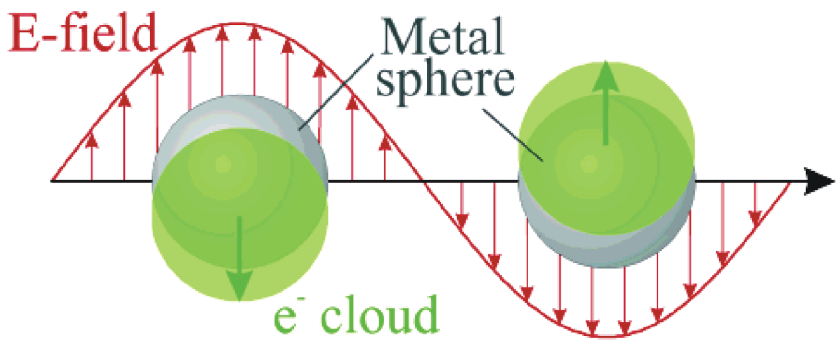
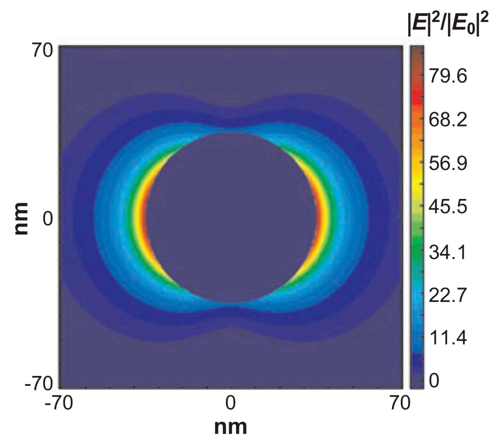


Coherent oscillatory motion



Resonant excitation



Colors in nanometals

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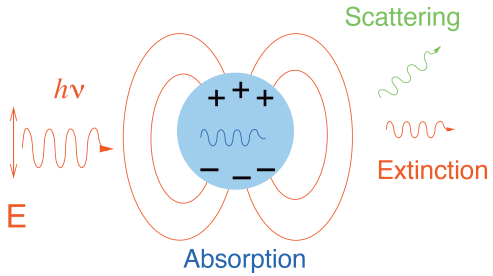

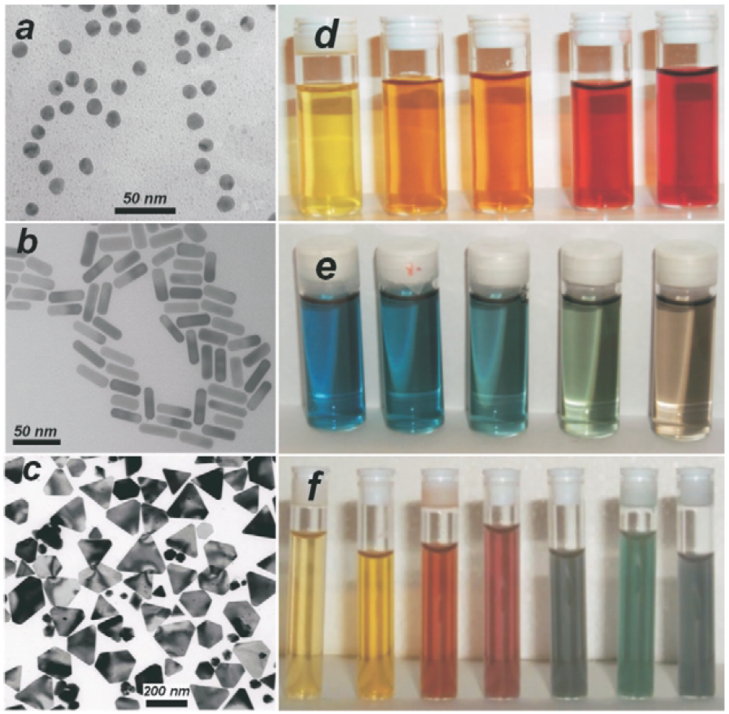

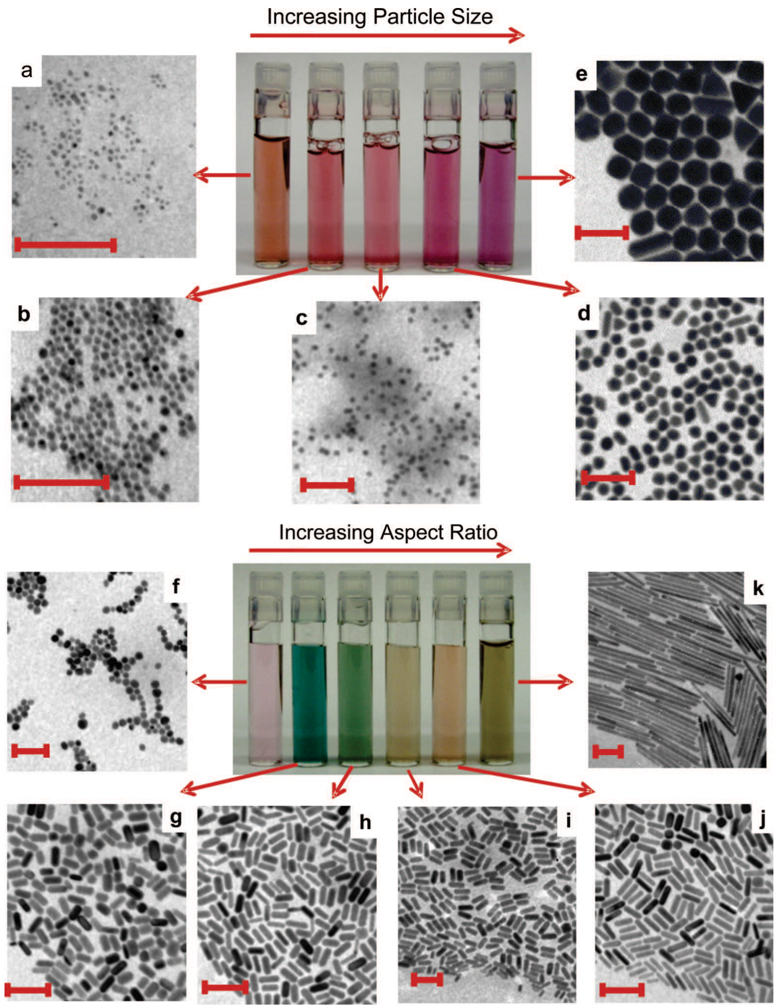

L. M. Liz-Marzan, Materials Today ***26****, February 2004; M. Pelton et al., Laser & Photon Rev. (in press), C. J. Murphy et al., Acc. Chem. Res. (in press).*