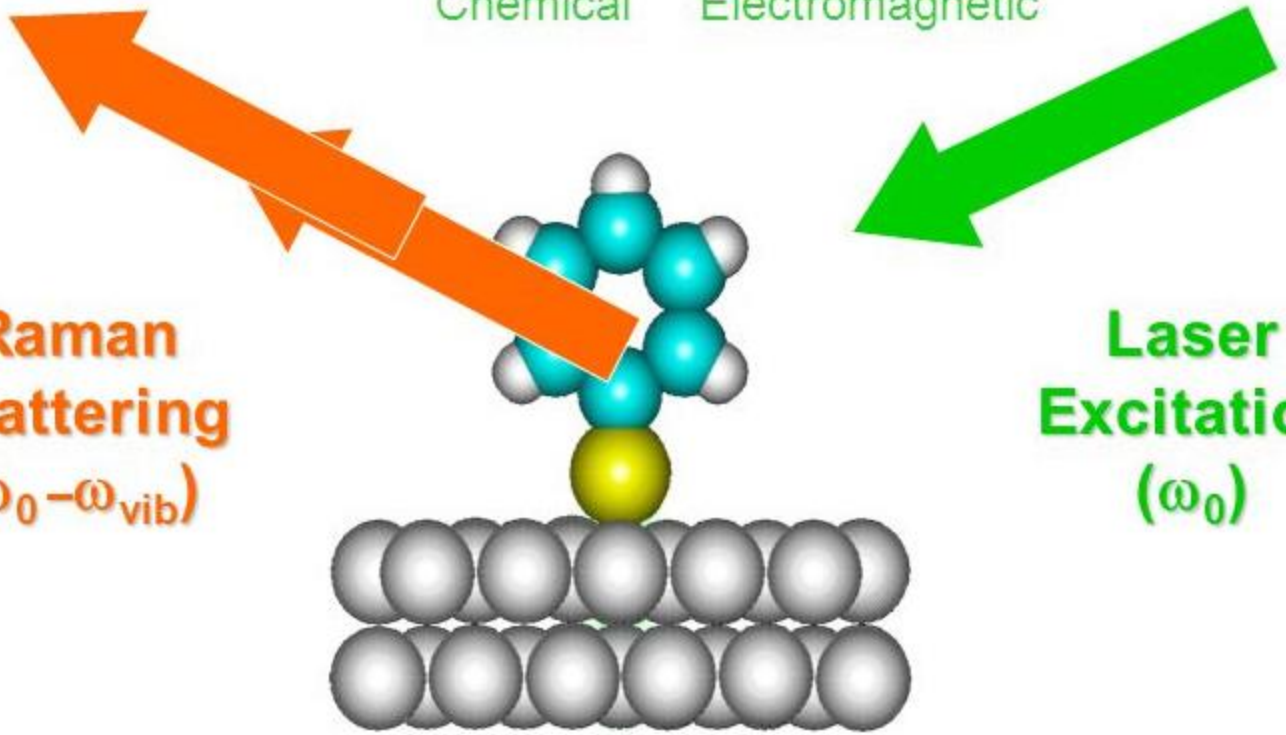
Surface-Enhanced Raman Scattering (SERS)

$$\text{Enhancement Factor (EF)} = \frac{\sigma_{SERS}}{\sigma_{Raman}}$$

$$\vec{\mu} = \hat{\alpha}\vec{E}$$

Chemical Electromagnetic



SERS Enhancement Mechanisms

Chemical Mechanism:

Laser excites (a) new electronic states arising from chemisorption or (b) shifted or broadened adsorbate electronic states yielding a resonance condition.

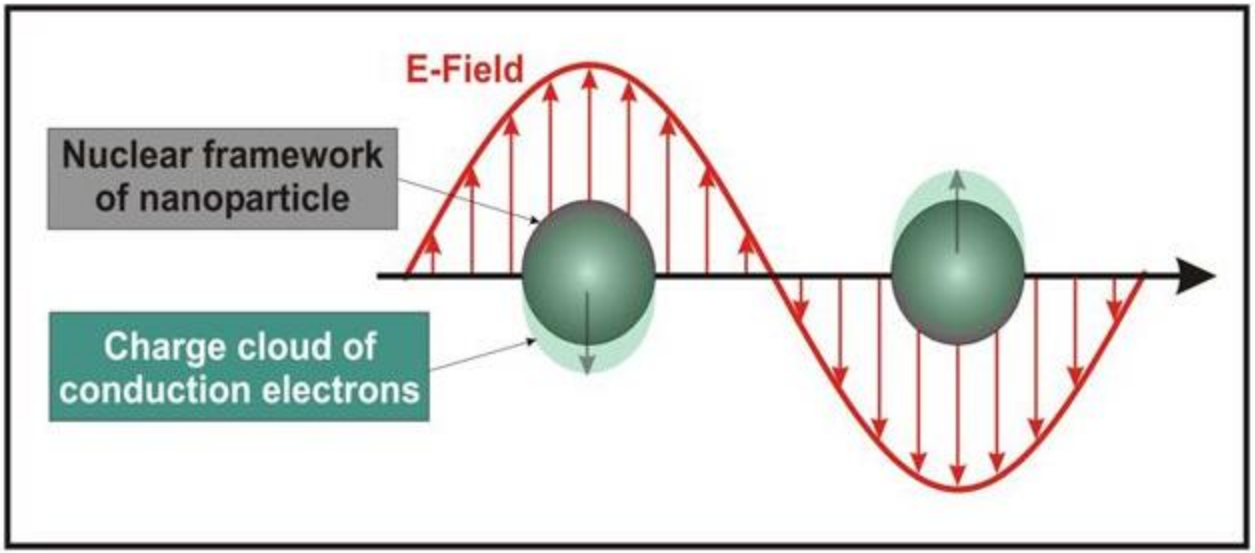
- Short range (1-5 Å)
- No roughness requirement
- Contributes EF ~ 10^2 – 10^4

Electromagnetic Mechanism:

LSPR induces large electromagnetic fields at roughened metal surface where molecules are adsorbed.

- Long range (2-4 nm)
- Affected by all factors determining LSPR
- Contributes EF > 10^4

Localized Surface Plasmon Resonance

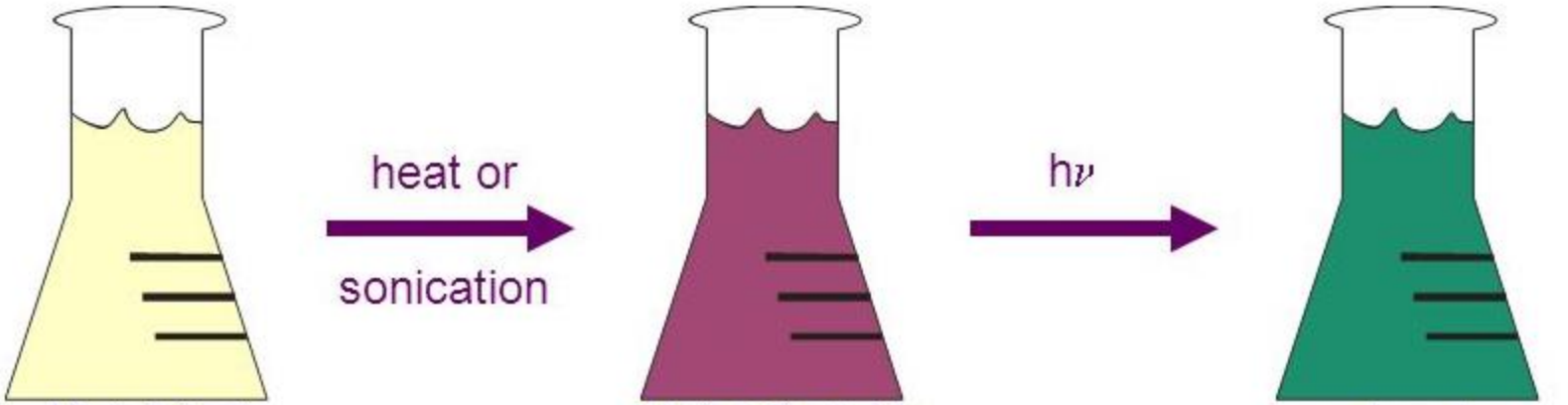


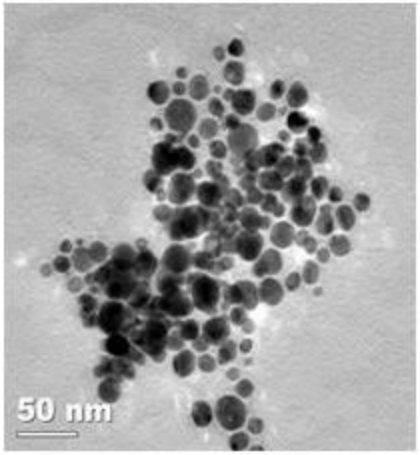
The resonance results in (1) wavelength-selective extinction and (2) enhanced EM fields at the surface.

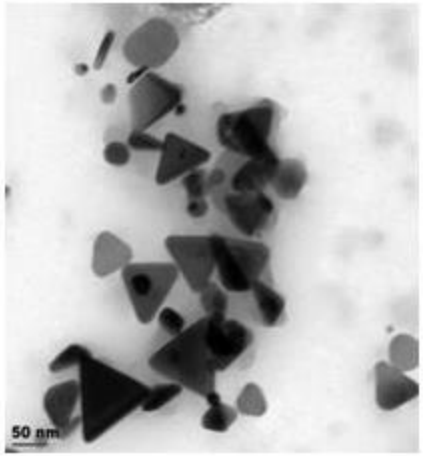
Spectral location of the LSPR is dependent upon particle size, shape, composition, and dielectric environment.

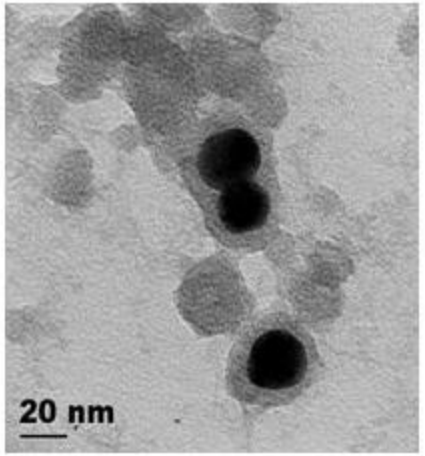
$$Extinction = \frac{24\pi^2 N a^3 \varepsilon_m^{3/2}}{\lambda \ln(10)} \left[\frac{\varepsilon_I}{(\varepsilon_R + 2\varepsilon_m)^2 + \varepsilon_I^2} \right]$$

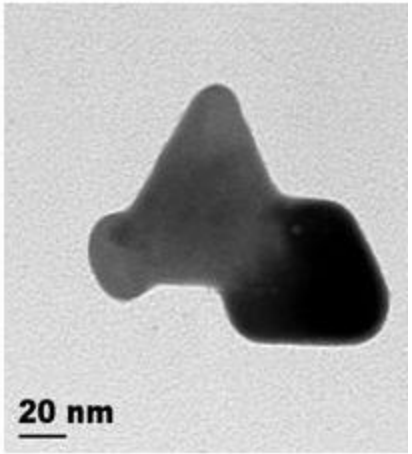
Noble Metal Nanoparticles







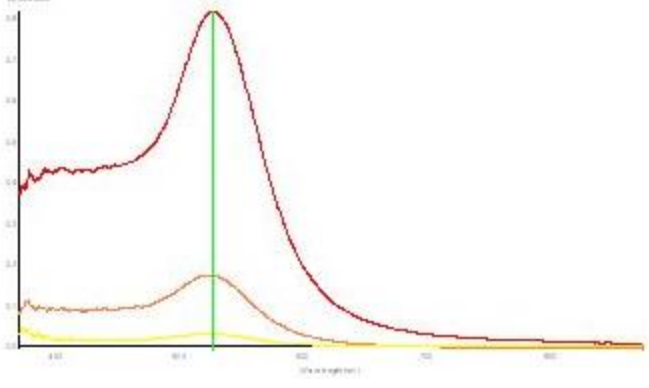




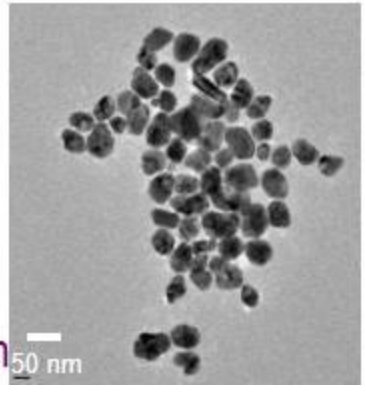
Noble Metal Nanoparticles

Row #	Metal	Reducing Agent	Capping Agent	Reaction Initiation	Extinction λ_{max} (nm)
1	Ag	$NaBH_4$/citrate[1]	citrate[1]	heat	397
2	Ag	EG[4]	EG[4]	sonication	441
3	Ag	EG[4]/PVP[5]	PVP[5]	sonication	451
4	Ag	EG[4]	BSPP[6]	sonication	468
5	Au	PVP[5]/DMF[3]	PVP[5]	sonication	513
6	Au	citrate[1]	citrate[1]	heat	520
7	Au	EG[4]/ PVP[5]	PVP[5]	sonication	530
8	Au	PVP[5]	PVP[5]	sonication	542
9	Au	tartrate[2]/ citrate[1]	tartrate[2]/ citrate[1]	sonication	543
10	Au	citrate[1]	citrate[1]	sonication	545
11	Au	EG[4]	BSPP[6]	sonication	554
12	Au	tartrate[2]	tartrate[2]	sonication	575
13	Au	citrate[1]	PVP[5]	heat	580

[1]citrate = $Na_3C_6H_5O_7$; [2]tartrate = $KO_2CCH(OH)CH(OH)CO_2H$; [3]*N,N*-dimethylformamide (DMF) = $HCON(CH_3)_2$;
[4]ethylne glycol (EG) = $HOCH_2CH_2OH$; [5]polyvinylpyrrolidone (PVP) = $(C_6H_9NO)_n$;
[6]bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium (BSPP) = $C_6H_5P(C_6H_4SO_3K)_2.2H_2O$



D = 24.8 ± 4.1 nm



Nanostructured Substrates

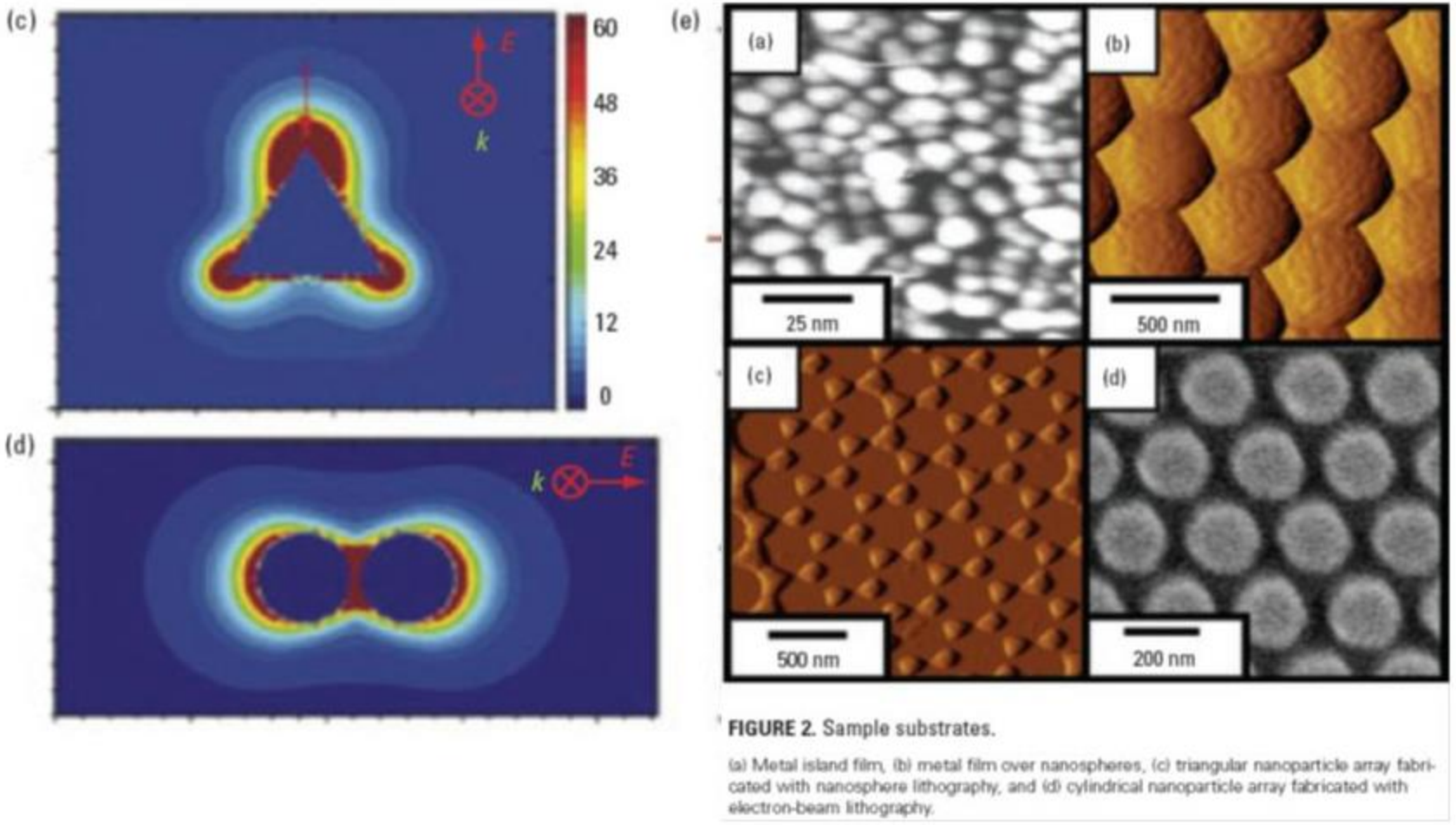
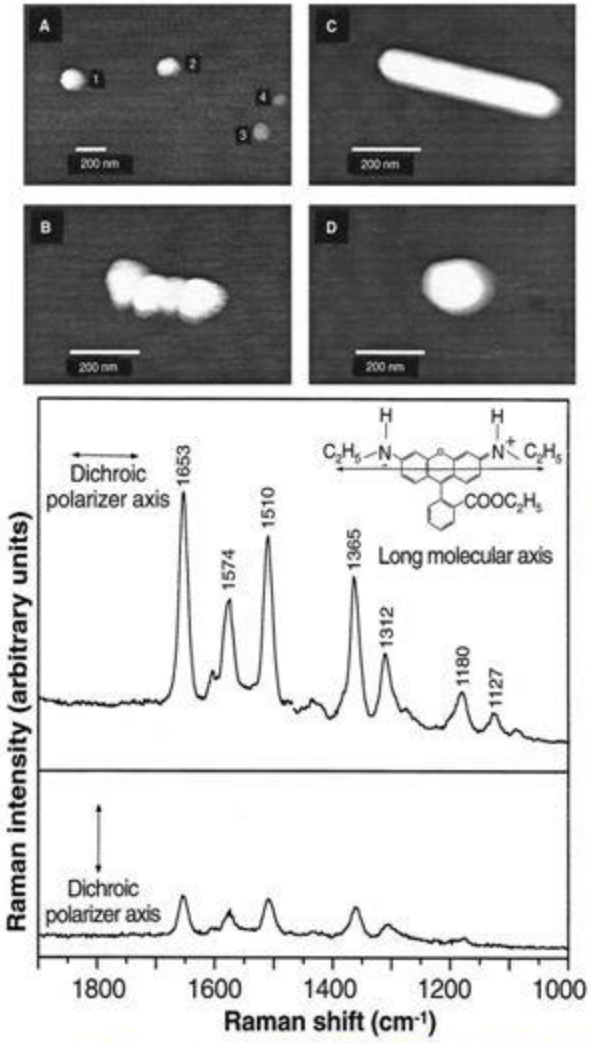


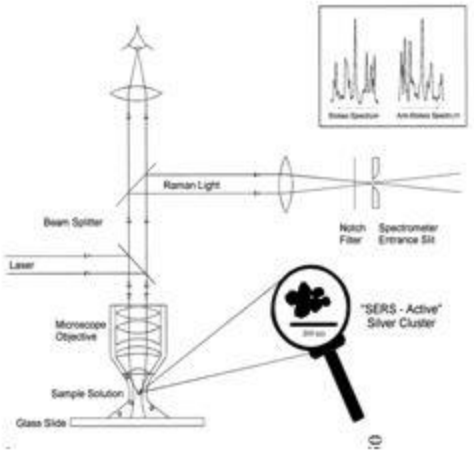
FIGURE 2. Sample substrates.

(a) Metal island film, (b) metal film over nanospheres, (c) triangular nanoparticle array fabricated with nanosphere lithography, and (d) cylindrical nanoparticle array fabricated with electron-beam lithography.

http://pubs.acs.org/cgi-bin/article.cgi/ancham-a/0000/77/i17/pdf/905feature_vanduyne.pdf

Single Molecule SERS





EF= 10^{14}-10^{15} !

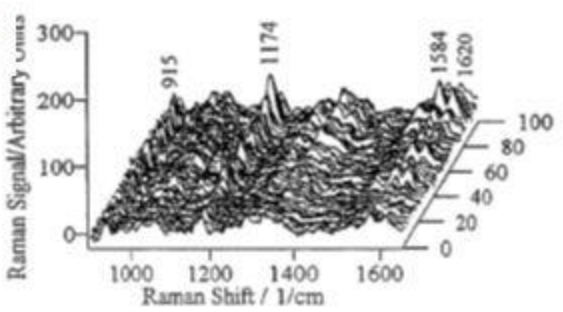
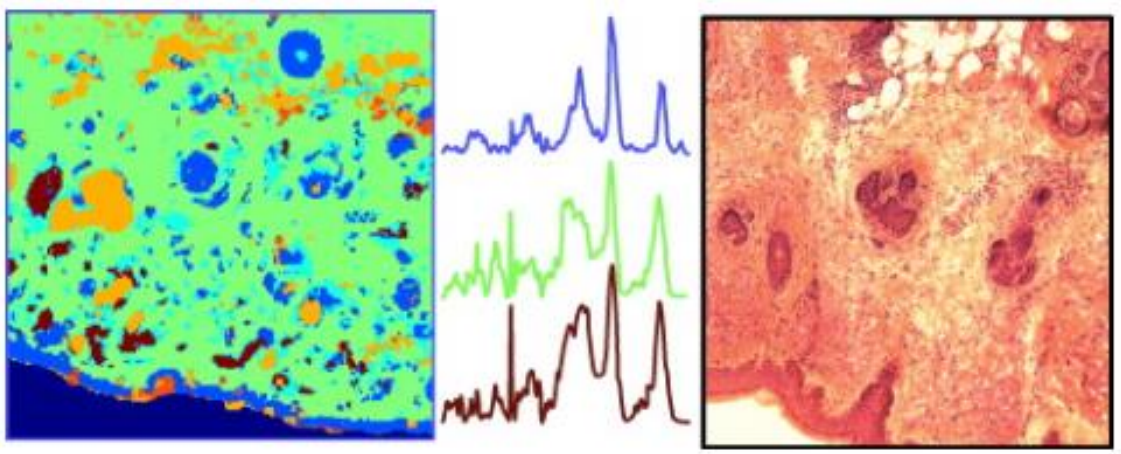


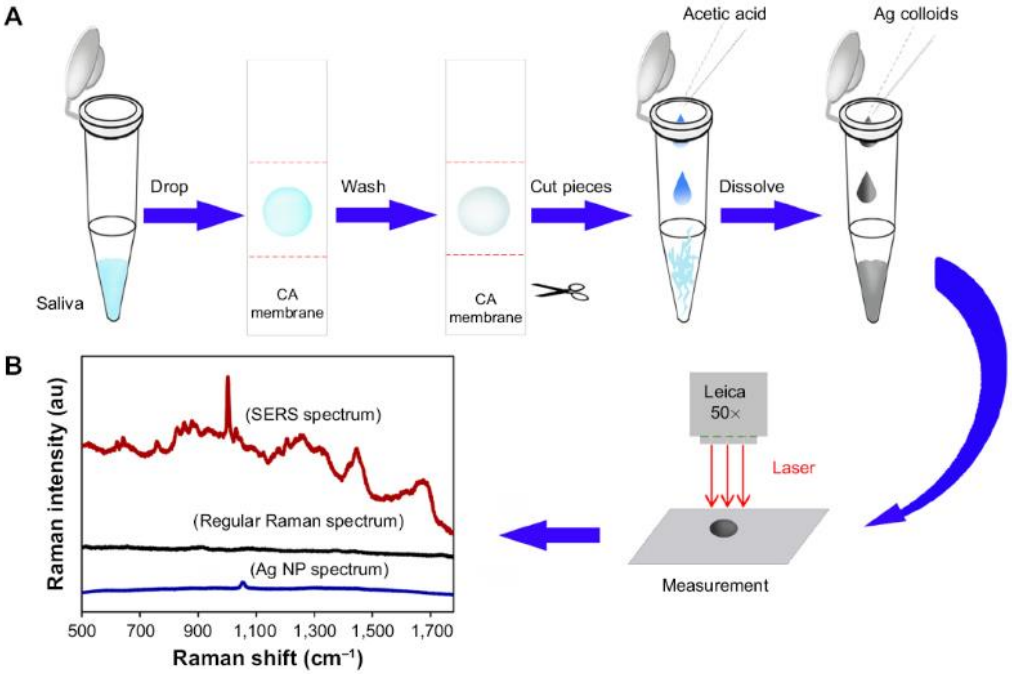
FIG. 1. 100 SERS spectra collected from a 30 pl scattering volume containing an average of 0.6 crystal violet molecules, displayed in the time sequence of measurement. Each spectrum is acquired in 1 second.

S. Nie, et. al. *Science* 1997, 275, 1102-1106 K. Kneipp, et. al. *Phys. Rev. Lett.* 1997, 78, 1667-1670

Medical applications

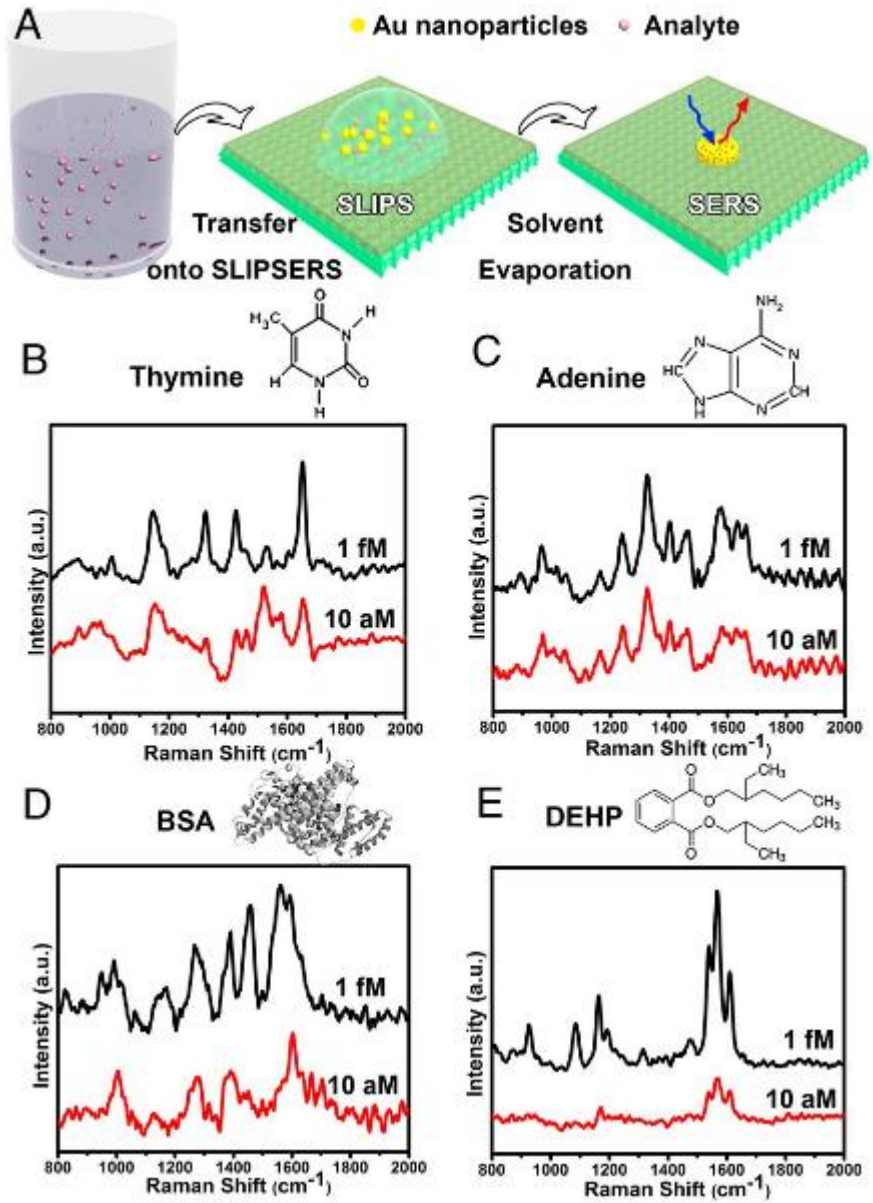


Cancer detection

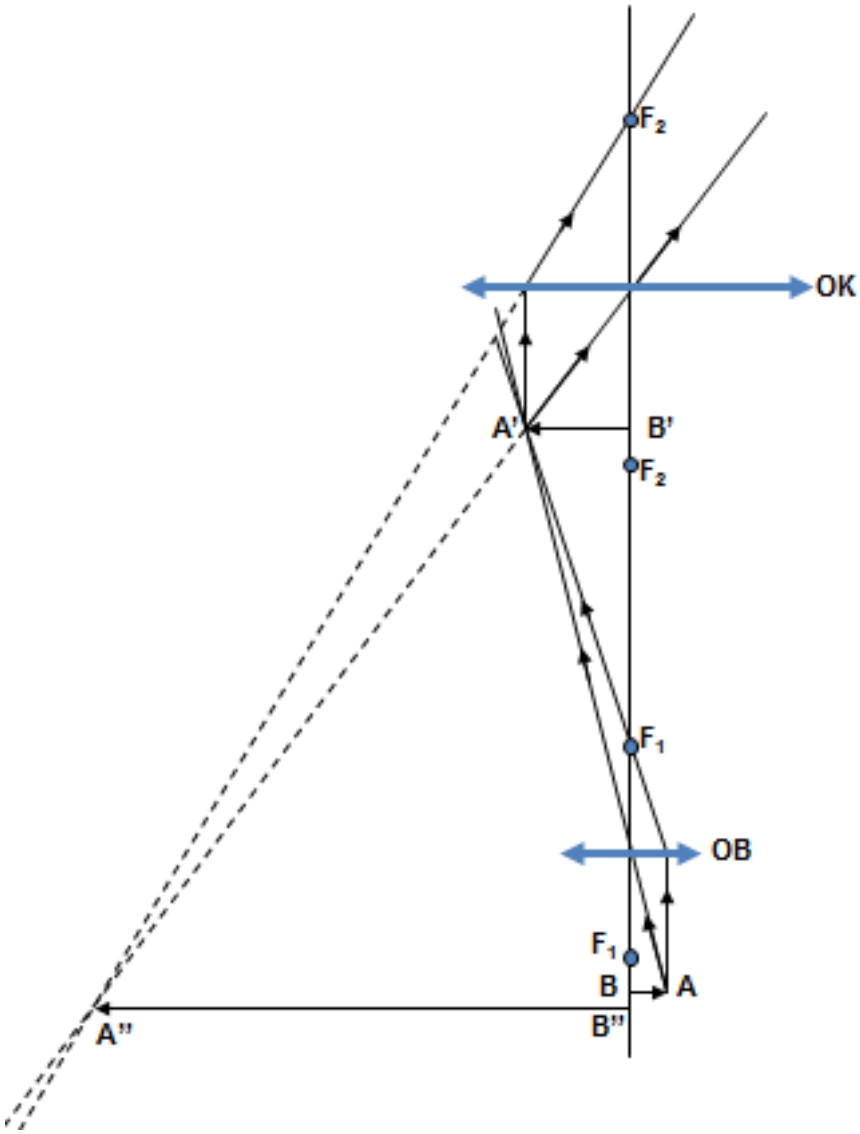


Differentiation of benign and malignant breast tumors

Medical applications



Amino acids detection


F2
OK
A'
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F2
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OB
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