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Enhancement of electromagnetic field by metal nanostructures. Surface enhanced spectroscopy

1. Introduction

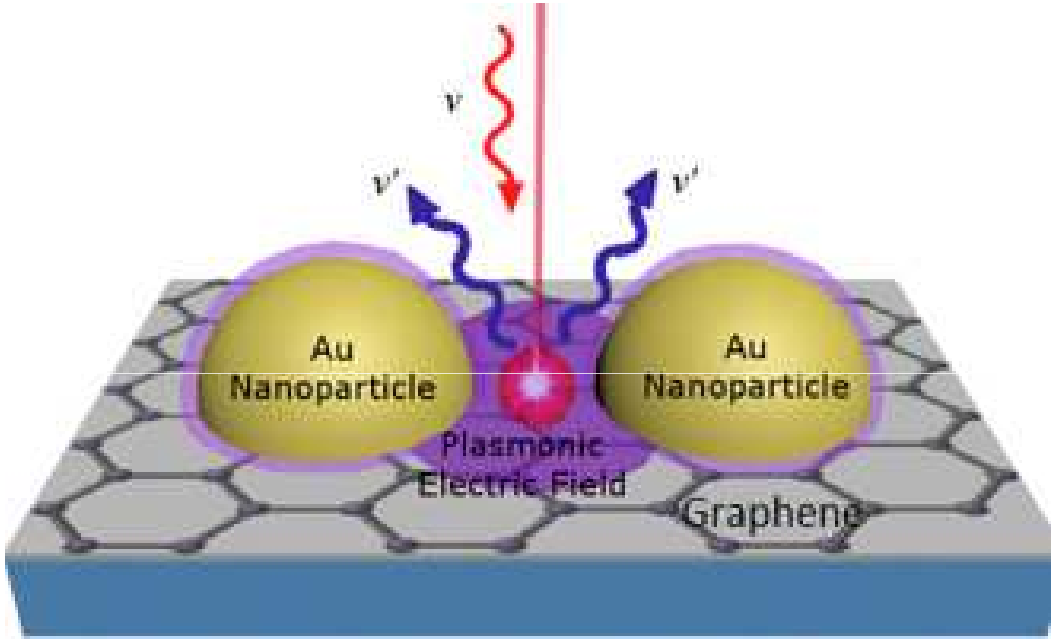
The surface plasmons are the electronic eigenmodes of the metal nanoparticles. When the frequency of the external light wave is in resonance with SPR frequency of nanoparticle the strong resonant increase of the surface plasmon oscillations of the free electrons occur.

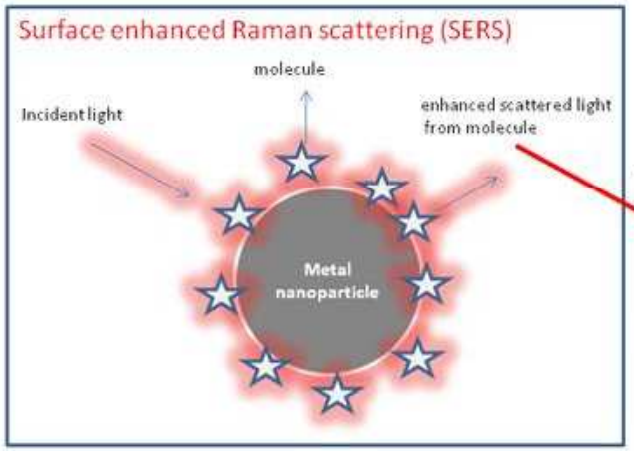
The SPR causes the generation of the strong EM field near the surface of the nanoparticles – plasmonic enhancement of EM field. The induced optical transitions in quantum system (molecules, nanoparticles, clusters, etc.) located in such plasmonic field are strongly enhanced.

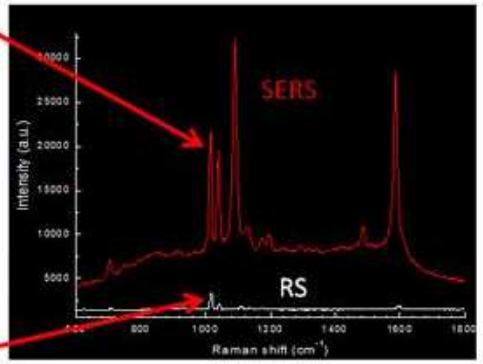
This enhancement is a physical background of various methods of surface enhanced spectroscopy:

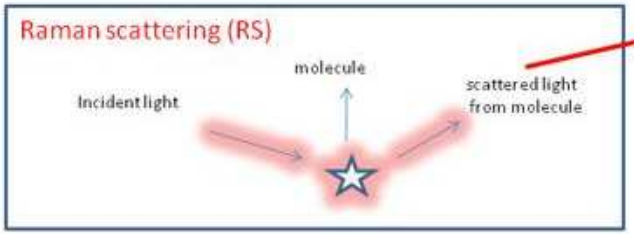
1. SERS – surface enhanced Raman scattering;
2. SEPL – surface enhanced photoluminescence;
3. SEIRA – surface enhanced infrared absorption;
4. Surface enhanced non-linear optical processes, e.g. SESHG – surface enhanced second harmonic generation, SETPA – surface enhanced two-photon absorption;
5. Surface enhanced photoluminescence of the metal nanoparticles (very exotic phenomenon).
6. Etc.

Plasmonic enhancement - outline

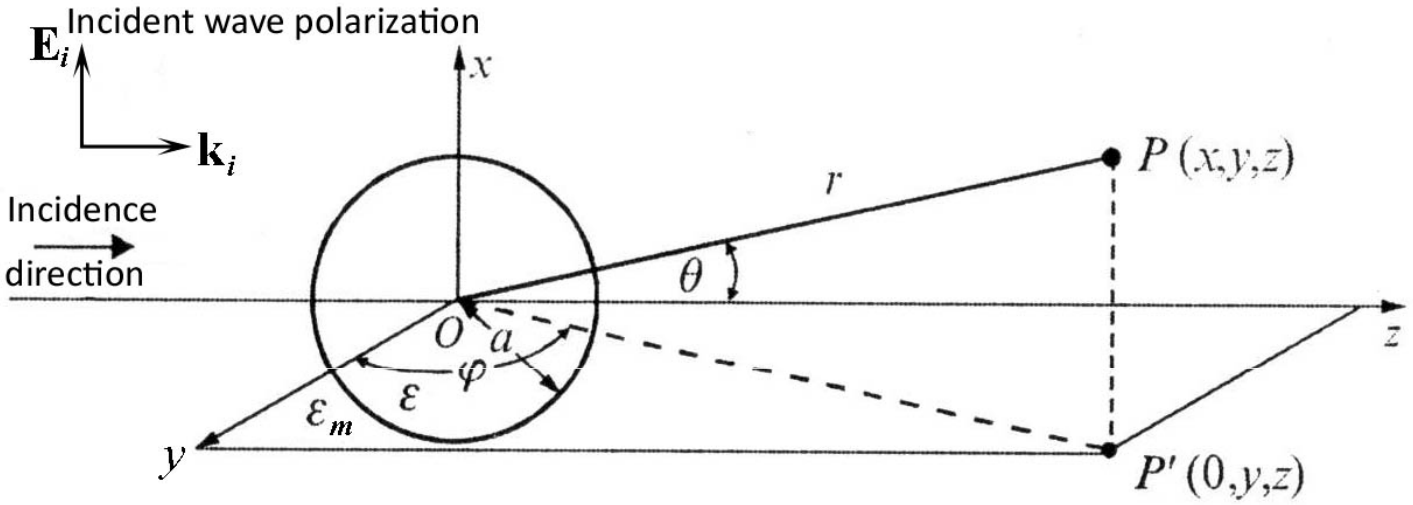








2. Theory of plasmonic enhancement



The potential of plasmonic dipole excited in the nanoparticle of radius *a* at a distance *r* from the center of NP:

$$\varphi(\mathbf{r}) = -\delta_{l,1}\delta_{m,0}E_0 a\left[\left(\frac{r}{a} - \frac{\varepsilon-\varepsilon_m}{\varepsilon+2\varepsilon_m}\frac{a^2}{r^2}\right)\eta(r-a) + \right.$$

$$\left. + \frac{3\varepsilon_m}{\varepsilon+2\varepsilon_m}\eta(a-r)\cos\theta\right],$$

$$\eta(x) = \begin{cases} 0, & x<0; \\ 1, & x\geq 0 \end{cases}$$ - Heaviside function; E_0 - amplitude of incident wave

Electric field outside the nanoparticle:

$$\mathbf{E} = -\nabla\varphi \quad \Rightarrow \quad E_i(\omega,\mathbf{r}) = E_{0i}(\omega) + u_{ij}(\mathbf{r})\, d_j(\omega),$$

where $d_i(\omega) = \alpha(\omega) E_{0i} = a^3 \dfrac{\varepsilon(\omega)-\varepsilon_m}{\varepsilon(\omega)+2\varepsilon_m} E_{0i}$, $u_{ij}(\mathbf{r}) = \dfrac{3r_i r_j - \delta_{ij} r^2}{r^5}$.

The local field enhancement factor is: $g(\omega,\mathbf{r}) = \left| \dfrac{E(\omega,\mathbf{r})}{E_0(\omega)} \right|$

Correspondingly, the amplitude and energy factors of field enhancement outside the NP is:

$$g_{out}(\omega_{sp}, a) \approx 3 \frac{|\varepsilon_1(\omega_{sp})|}{\varepsilon_2(\omega_{sp})}, \qquad g_{out}^2(\omega_{sp}, a) \approx 9 \left(\frac{|\varepsilon_1(\omega_{sp})|}{\varepsilon_2(\omega_{sp})} \right)^2$$

The amplitude and energy factors of field enhancement inside the NP is:

$$g_{in}\left(\omega_{sp},a\right)=\frac{\varepsilon_m}{\left|\varepsilon_1\left(\omega_{sp}\right)\right|}g_{out}\left(\omega_{sp},a\right)\approx 3\frac{\varepsilon_m}{\varepsilon_2\left(\omega_{sp}\right)}$$

$$g_{in}^2\left(\omega_{sp},a\right)\approx 9\left(\frac{\varepsilon_m}{\varepsilon_2\left(\omega_{sp}\right)}\right)^2$$

Conclusion: The higher enhancement is achieved by NPs of metals with smaller imaginary part of dielectric permittivity (lower damping of plasma oscillations). This condition is best realized in noble metals Ag and Au which are commonly used in plasmonic enhancement applications and devices.

Example: The 10 nm spherical silver NPs provide the enhancement of the absorption and photoluminescence processes of $g^2\approx 10^3$ and the enhancement of Raman scattering of $G=g^4\approx 10^6$ **(!)**

Huge enhancement provides possibility to measure the optical spectra from single molecules and particles – single particle spectroscopy.

2.1. Plasmonic enhancement: dependence on NP size

The enhancement factor depends on the NP size due to following mechanisms:

1. Scattering of the free electrons on the surface of NP – surface scattering.

Respectively, the metal dielectric permittivity is size dependent:

$$\varepsilon(\omega,a)=\varepsilon_1(\omega)+\varepsilon_2(\omega)\left[1+A\frac{l_\infty}{a}\right]$$

It is actual for small NPs (smaller than about 20-30 nm).

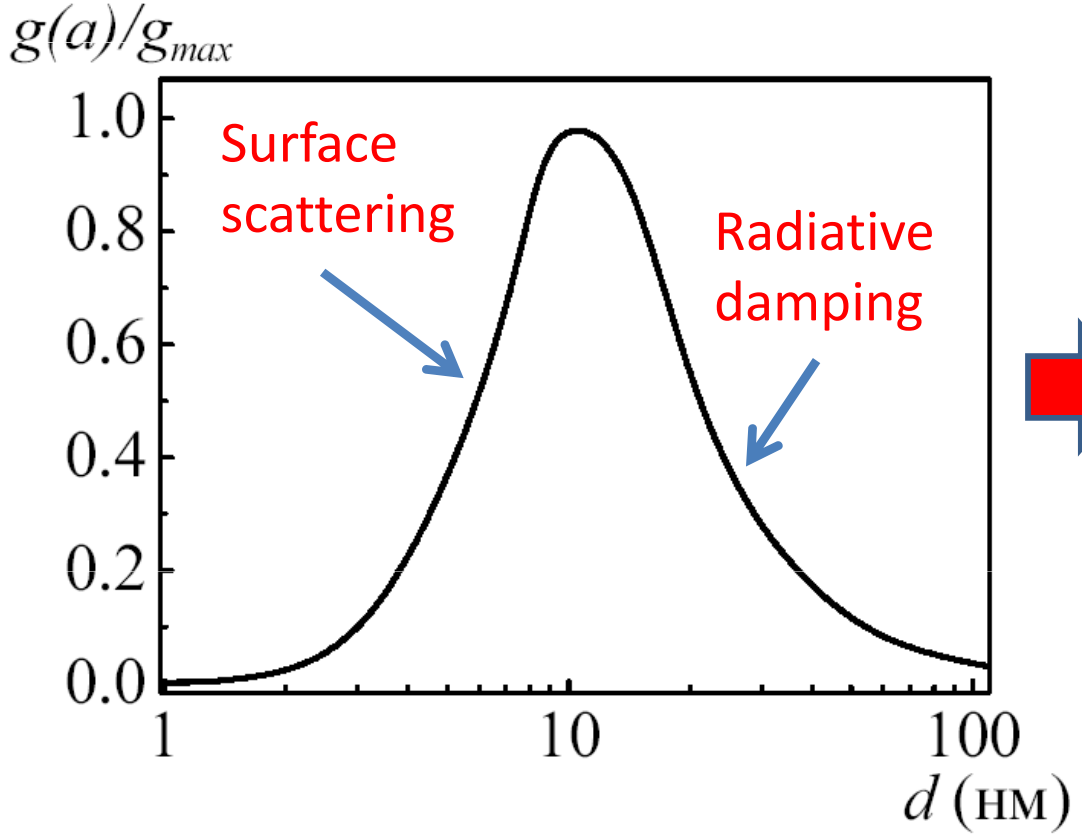
2. Radiative damping of the plasma oscillations. It is actual for large NPs (larger than about 80-100 nm).

The size dependent enhancement factor for the field inside the NP:

$$g_{in}(\omega,a)=\left|\frac{D^{-1}}{\frac{\varepsilon(\omega,a)}{\varepsilon_m}-1+D^{-1}\left[1+i\frac{4\pi^2V\left(1-\varepsilon(\omega,a)\right)}{3\lambda^3}\varepsilon_m^{\,1/2}\right]}\right|$$

The size dependent enhancement factor for the field inside the NP:

$$g_{out}(\omega,a)=\left|\frac{\varepsilon(\omega,a)}{\varepsilon_m}\right| g_{in}(\omega,a)=\left|\frac{\frac{\varepsilon(\omega,a)}{\varepsilon_m}D^{-1}}{\frac{\varepsilon(\omega,a)}{\varepsilon_m}-1+D^{-1}\left[1+i\frac{4\pi^2V\left(1-\varepsilon(\omega,a)\right)}{3\lambda^3}\varepsilon_m{}^{1/2}\right]}\right|$$



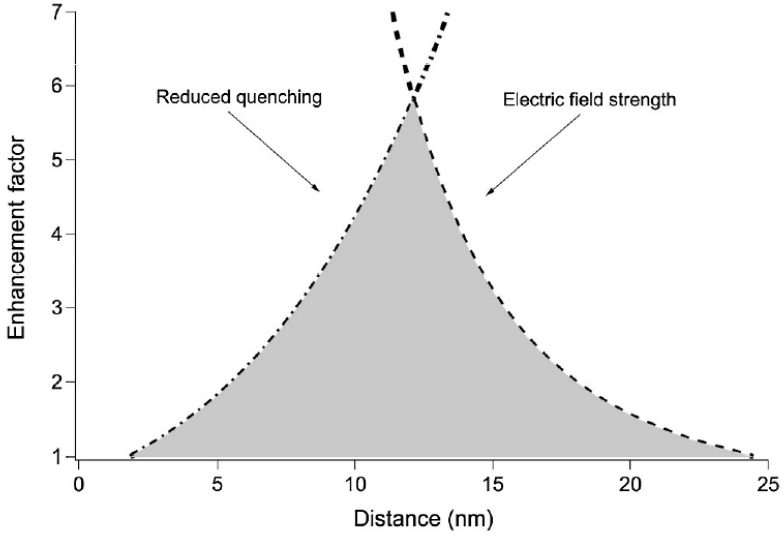
Characteristic NP size providing the maximal plasmonic enhancement exists: about 10 nm for Ag and Au NPs

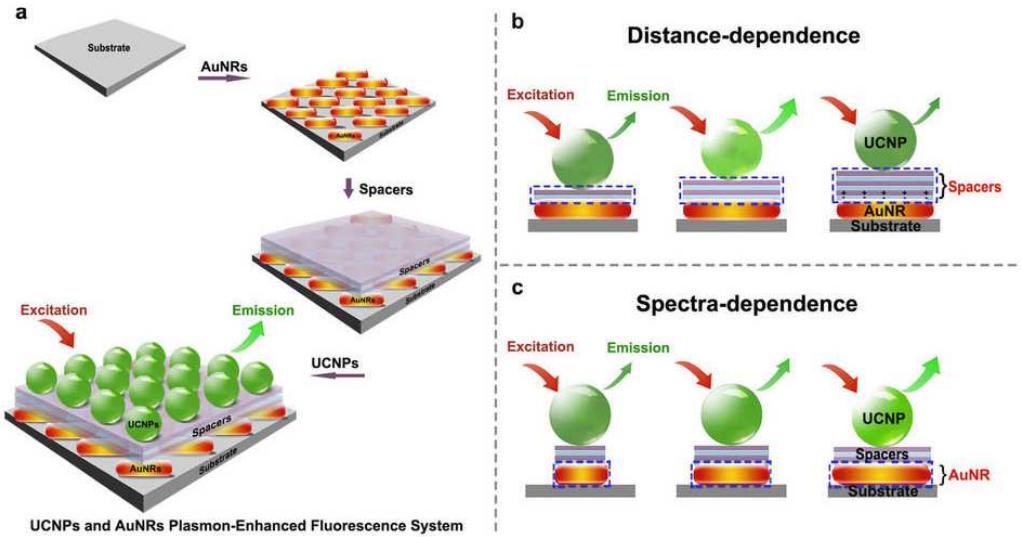
The size dependence of plasmonic enhancement factor for spherical silver NP

2.2. Plasmonic enhancement: dependence on distance to NP

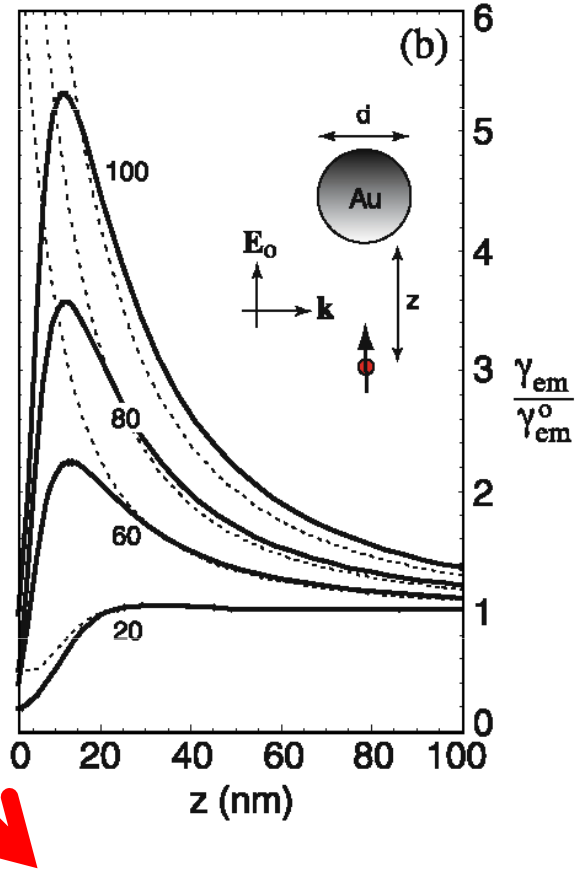
The enhancement factor depends on the distance from the molecule to NP due to following mechanisms:

1. FRET - Förster resonance energy transfer. Actual for small distances: 0-5 nm.
2. The plasmonic field strength decrease with increasing distance.





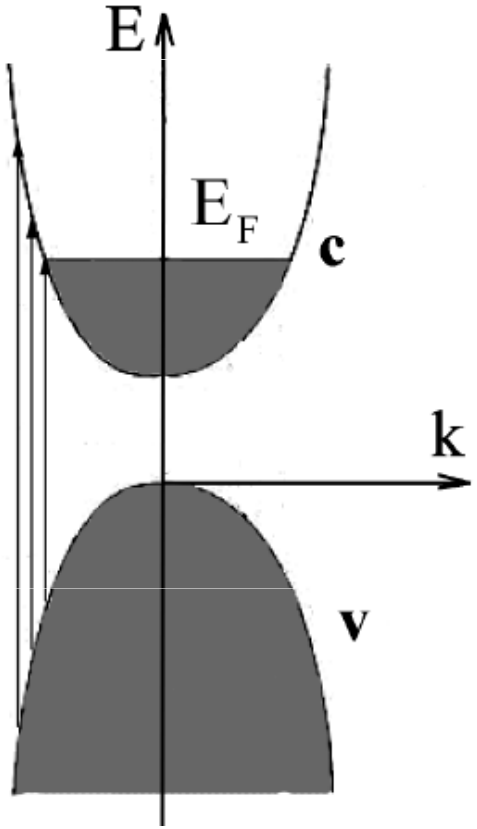
UCNPs and AuNRs Plasmon-Enhanced Fluorescence System

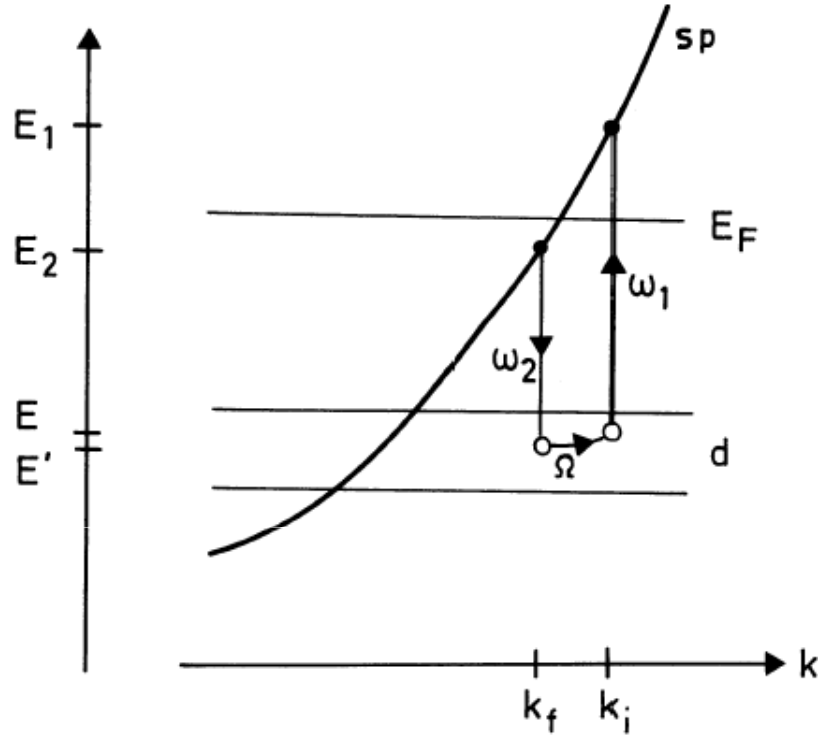


The plasmonic enhancement is maximal at optimal distances to the surface of NP: about 10-30 nm.

3. Photoluminescence of metal nanoparticles

The plasmonic field enhances not only the optical processes in external objects located outside the metal NP, but also the optical processes inside the NP itself. Most famous of the plasmonic enhanced optical processes in the metal NP is the photolumines-cence (PL). The quantum yield of bulk metals is very low (10^{-10}) that is due to absence of energy gap between the occupied and non-occupied electronic states.





PL of metals is experimentally observed near the interband absorption edge of the corresponding metal and originates from the direct radiative interband recombination of the conduction sp-band electrons with holes in the valence d-band that have been scattered to momentum states less than the Fermi momentum.

3.1. PL enhancement in metal nanoparticles: theory

The theory of plasmonic enhancement of PL from metal nanoparticles was developed by Boyd. According to the theory, the local electric field inside a particle is enhanced by the factor known as the local field correction factor:

$$L(\omega)=\frac{D^{-1}}{\varepsilon(\omega)-1+D^{-1}\left[1+i\frac{4\pi^2V(1-\varepsilon(\omega))}{3\lambda^3}\right]},$$

The intensity of PL from metal nanoparticle:

$$P(\omega_l)=2^4\beta(\omega_l)\left|E_0\right|^2V\left|L^2(\omega_{exc})L^2(\omega_l)\right|$$

The intensity of PL from smooth surface of bulk metal:

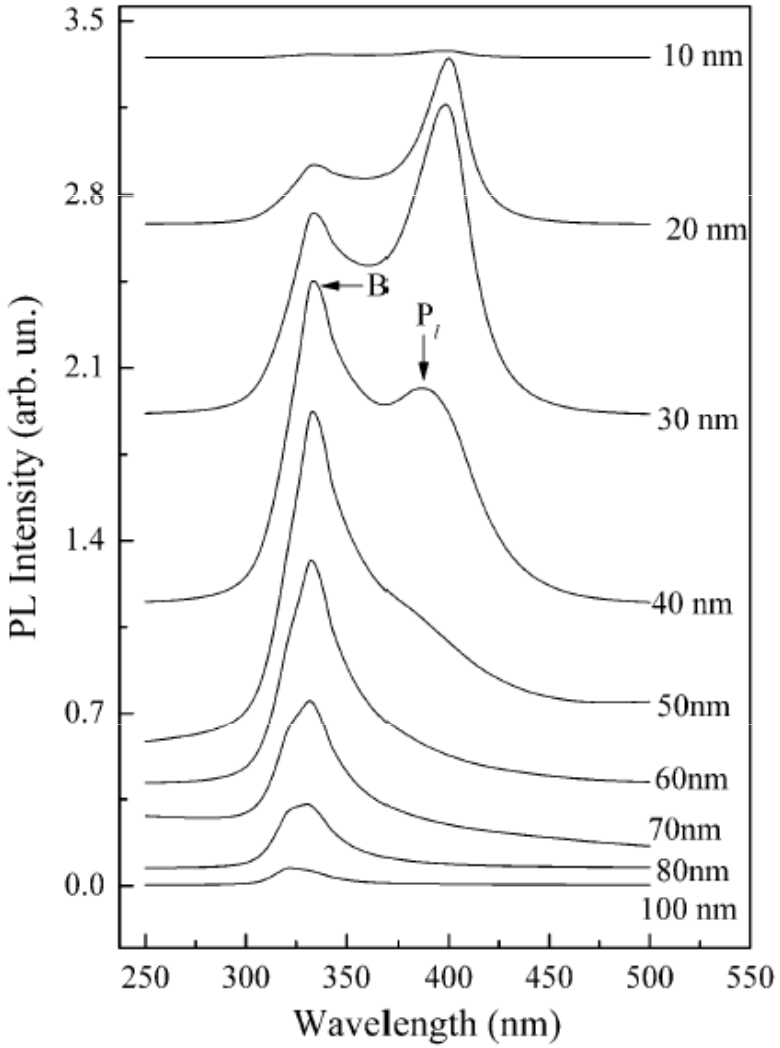
$$P_b(\omega_l)=\beta(\omega_l)\left|E_0\right|^2Sz_0(\omega_{exc},\omega_l)\left|L_b^2(\omega_{exc})L_b^2(\omega_l)\right|$$

where $z_0(\omega_{exc},\omega_l)=\left[\alpha(\omega_{exc})+\alpha(\omega_l)\right]^{-1}$ - effective absorption depth,

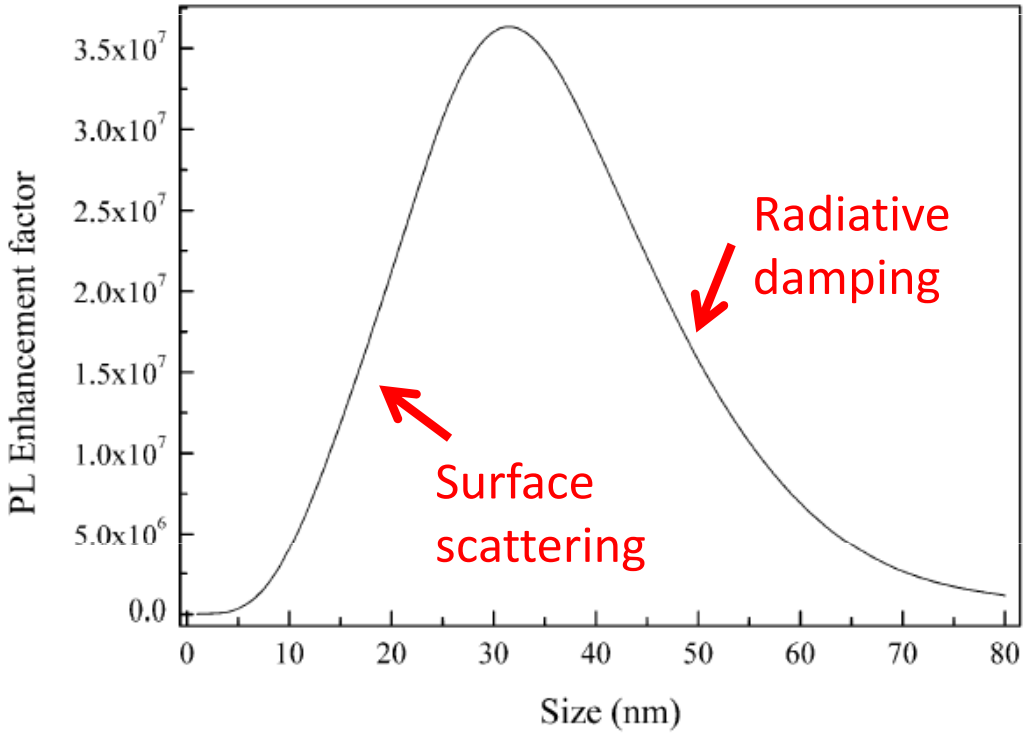
$L_b(\omega)=\frac{2\cos\theta}{\varepsilon^{1/2}(\omega)\cos\theta_0+\cos\theta}$ - Fresnel coefficient, $S=\pi d^2/4$ - NP cross-section

The enhancement factor of PL from metal nanoparticle:

$$\eta = \frac{P}{P_b} = 2^4 \frac{2d}{3z_0} \frac{\left|L^2(\omega_{exc})L^2(\omega_l)\right|}{\left|L_b^2(\omega_{exc})L_b^2(\omega_l)\right|}$$

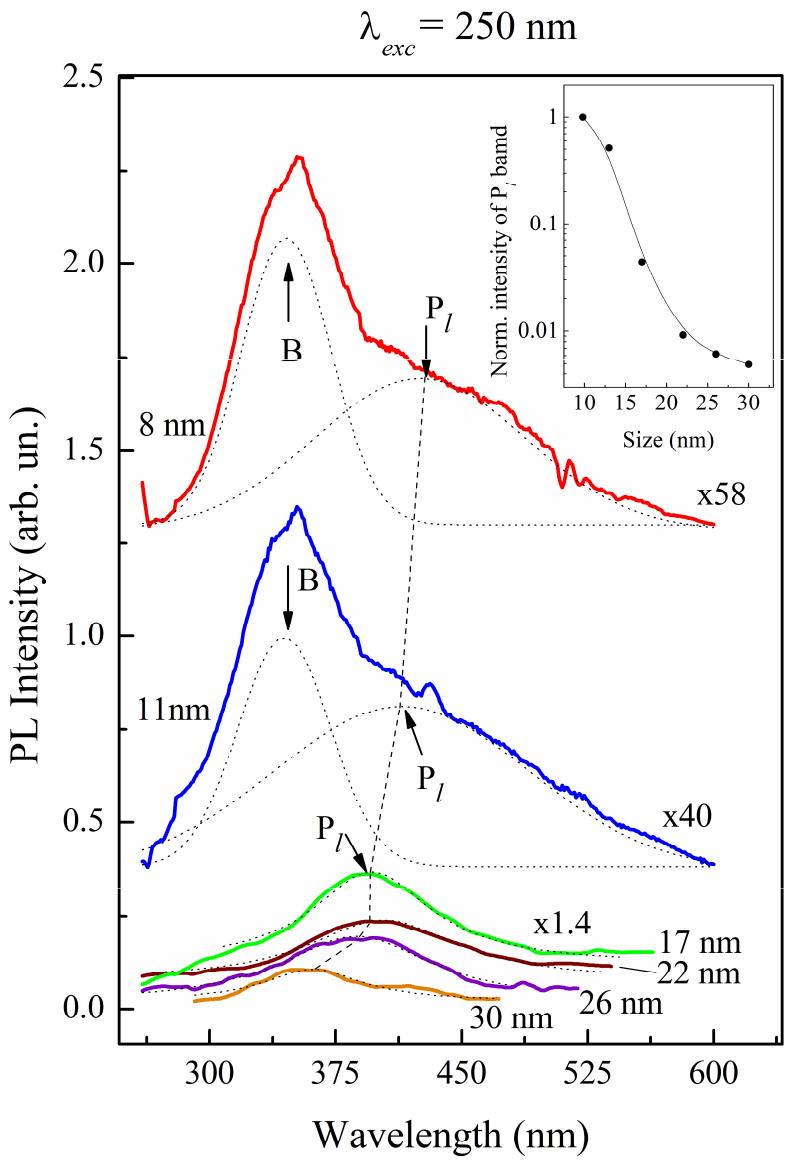


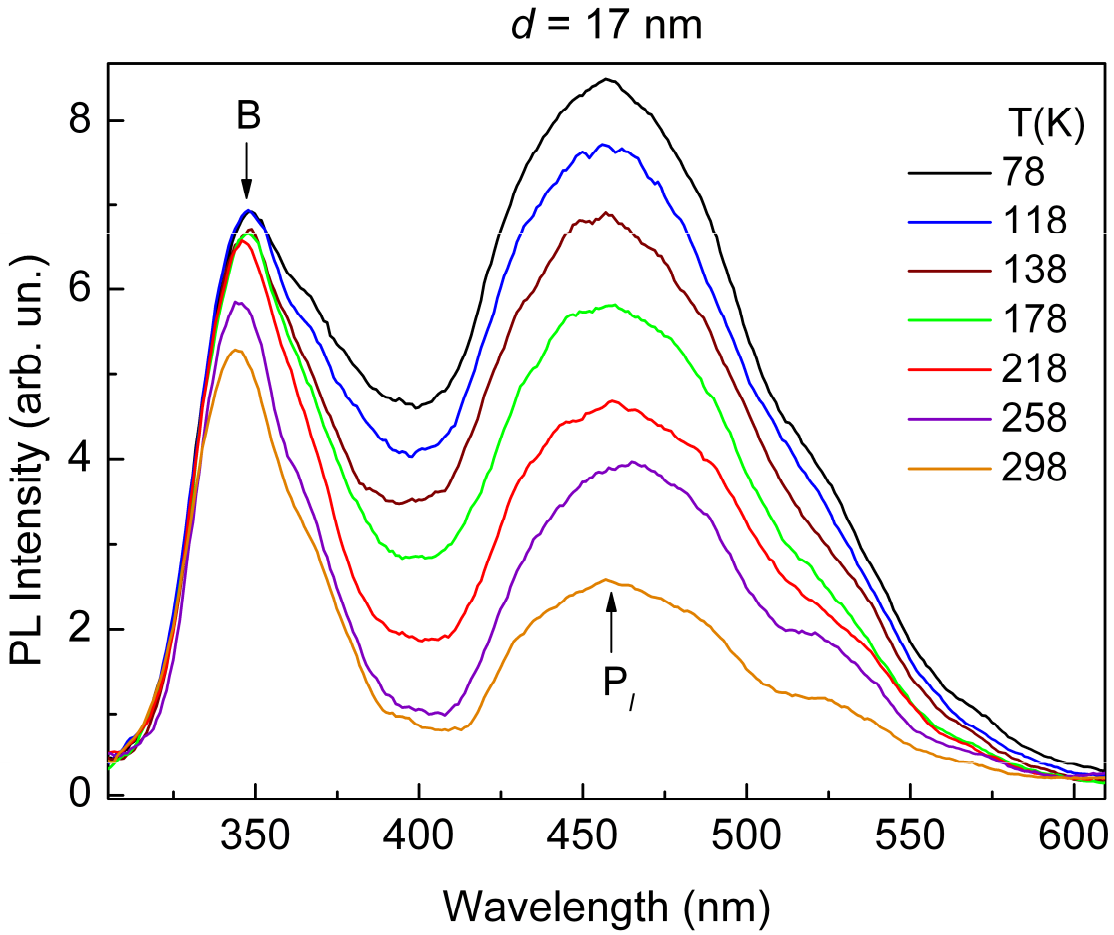
Calculated PL spectra of Ag NPs in quartz matrix for various size of NP



Calculated size dependence of enhancement factor of PL spectra of Ag NPs comparing to bulk Ag

Experimental PL spectra of spherical silver nanoparticles



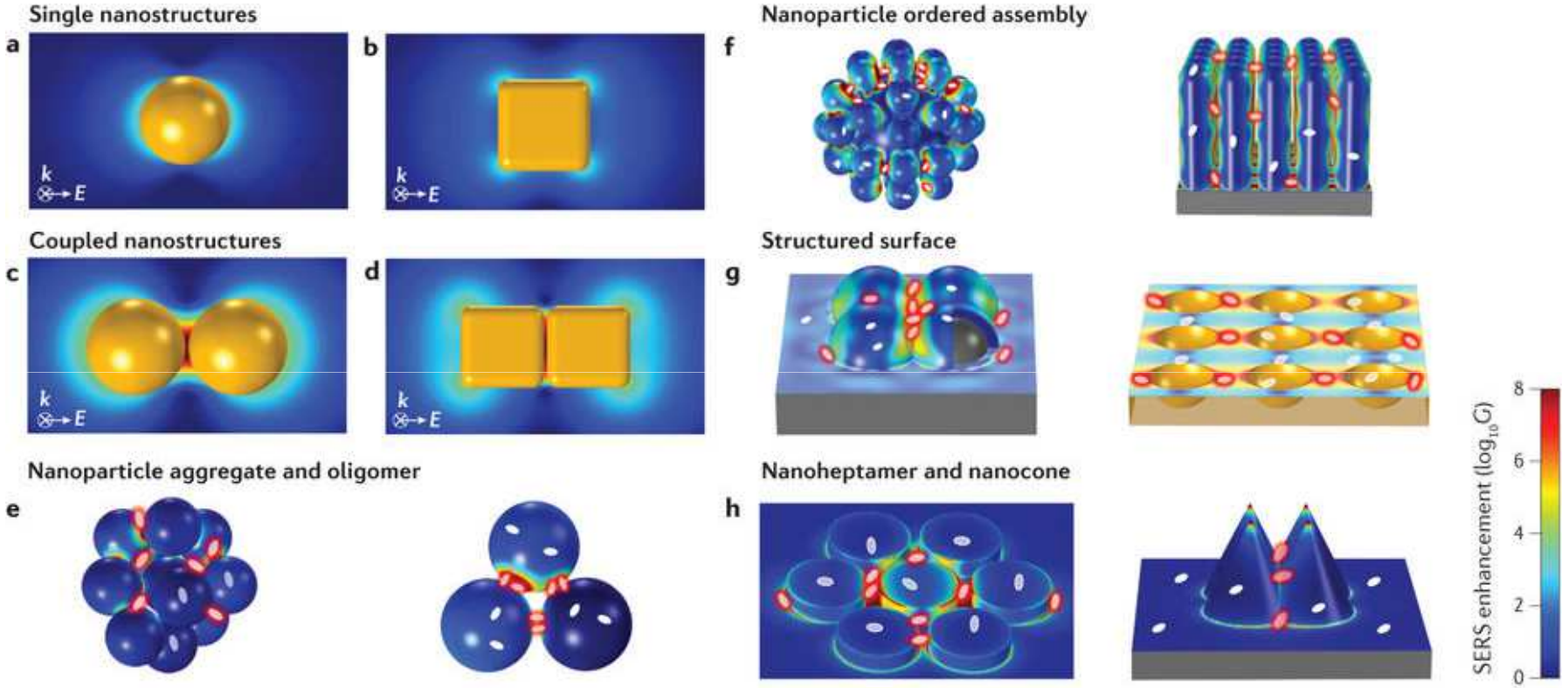


PL spectra of Ag NPs – dependence on size

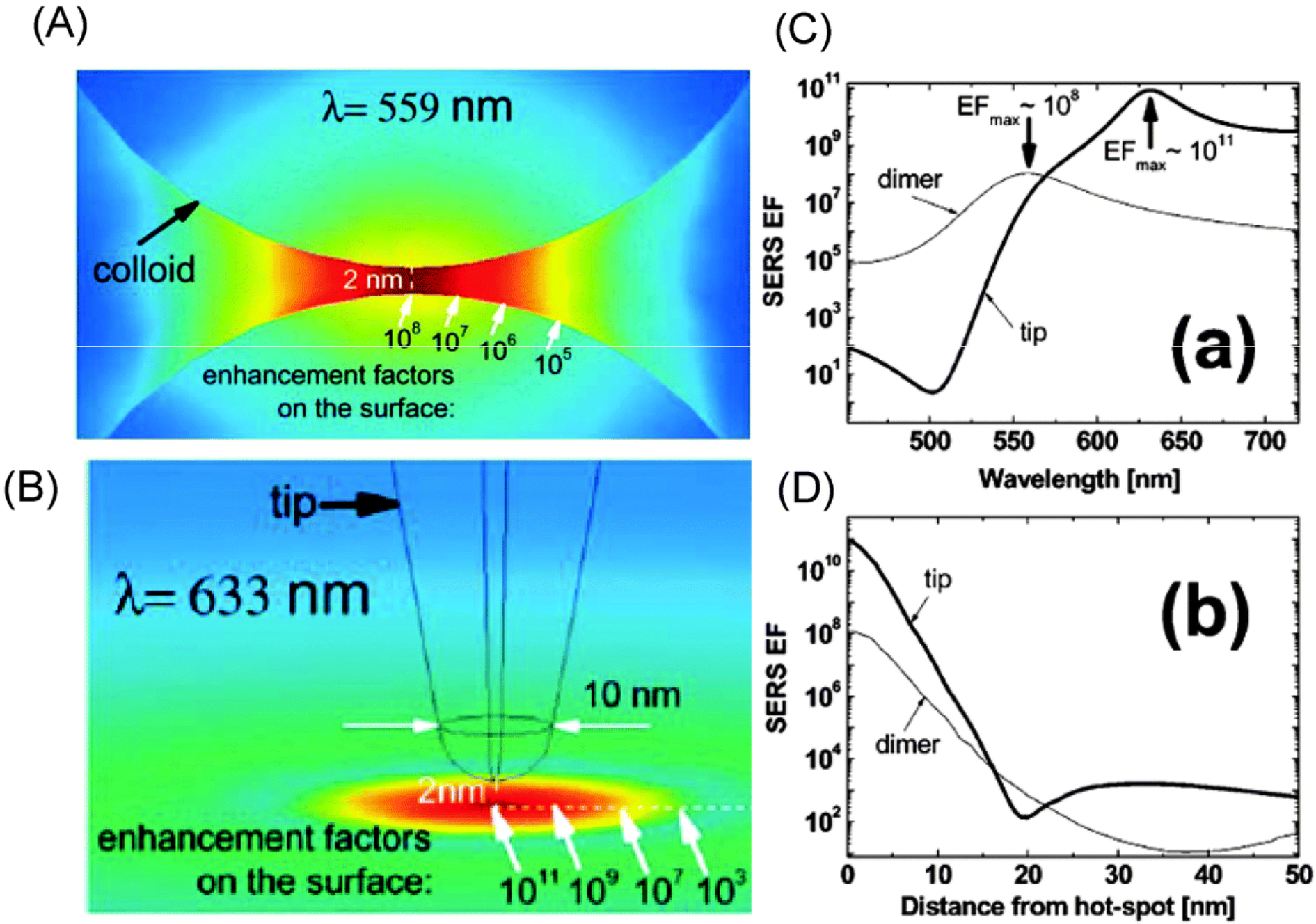
PL spectra of Ag NPs – dependence on temperature

4. Enhancement at high gradient field areas: hot spots

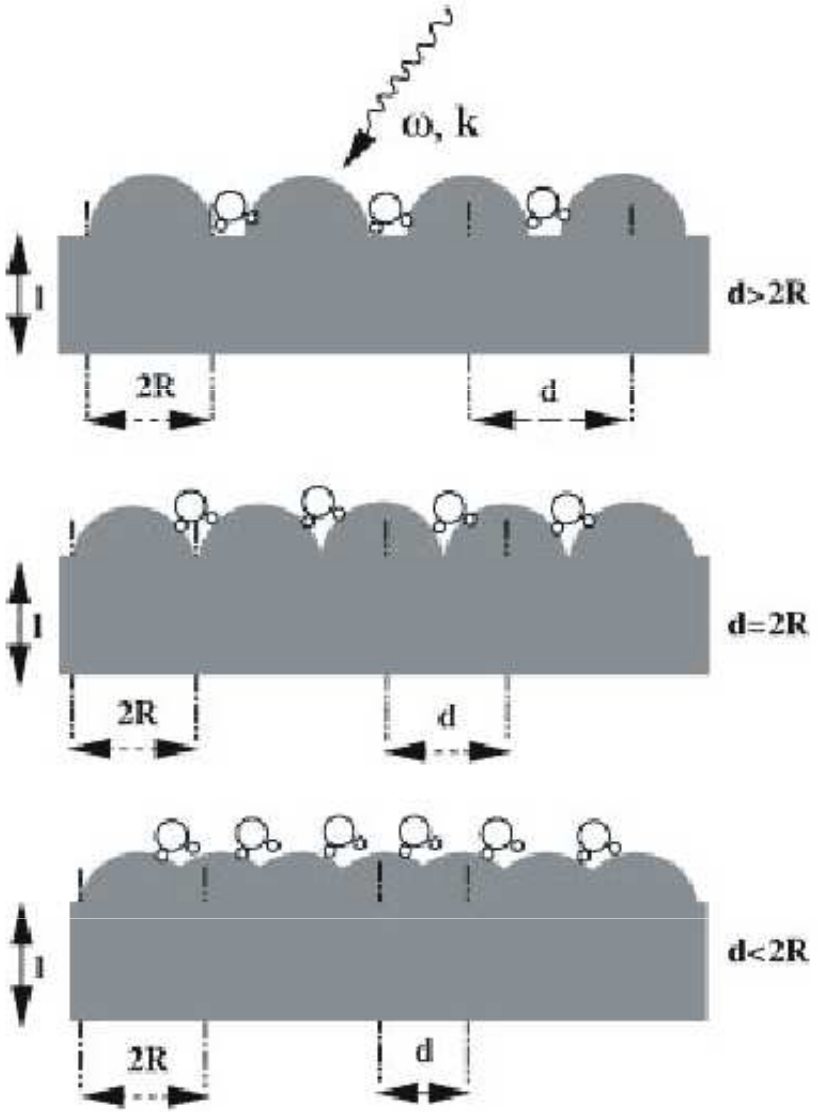
In order to achieve high local field enhancement, a metal nanostructures showing strong surface plasmons is desirable. Such condition is fulfilled in the spatial areas near the metal surface where the high gradient plasmonic field exists. The respective metal nanostructure would have the morphological features of the order of only a few nanometers: gaps, tips, edges, holes, etc. **Such area with high gradient electric field is called as "hot spots".**

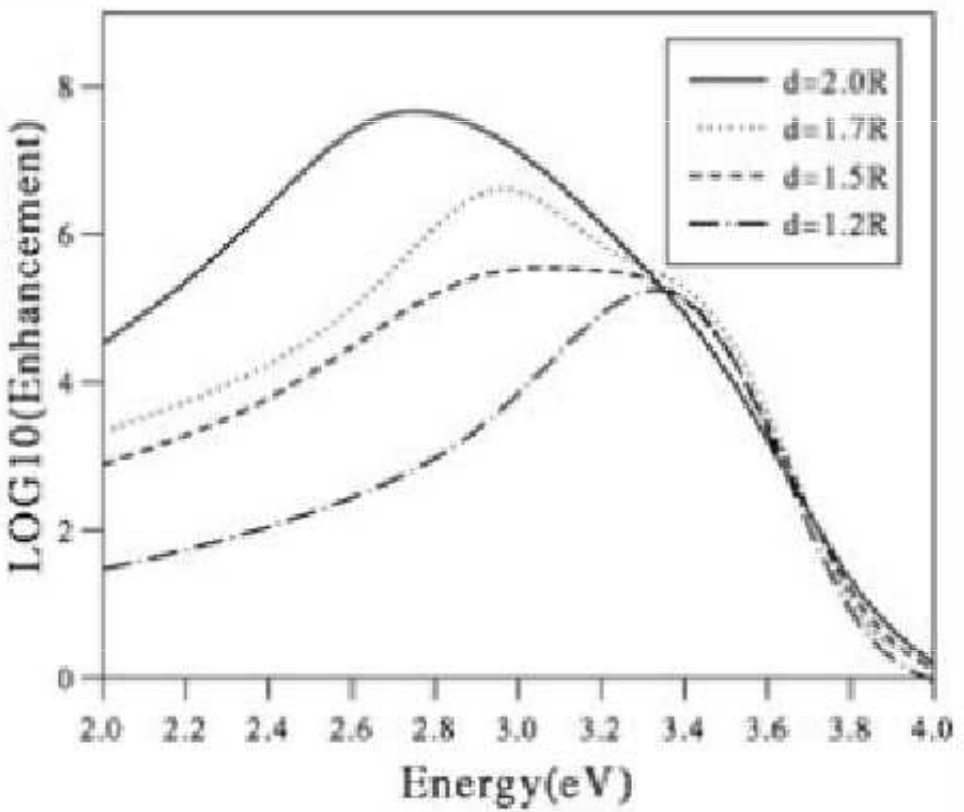


Various geometries of metal nanostructures providing hot spots for high plasmonic enhancement

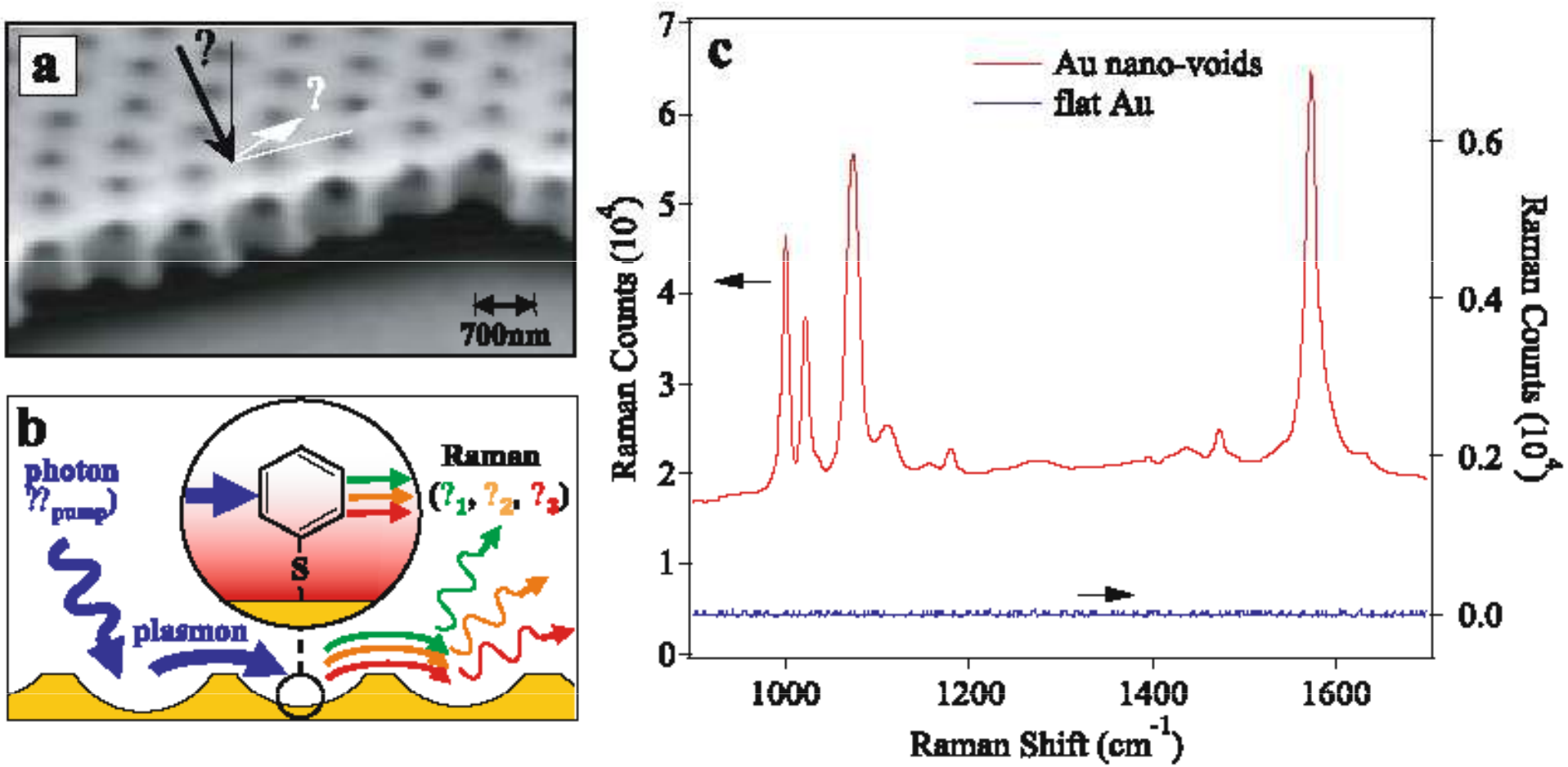


Spatial distributions and spectral dependences of enhancement factors achieved at hot spots in two-nanoparticle dimer and near the nanoscaled tip of STM.

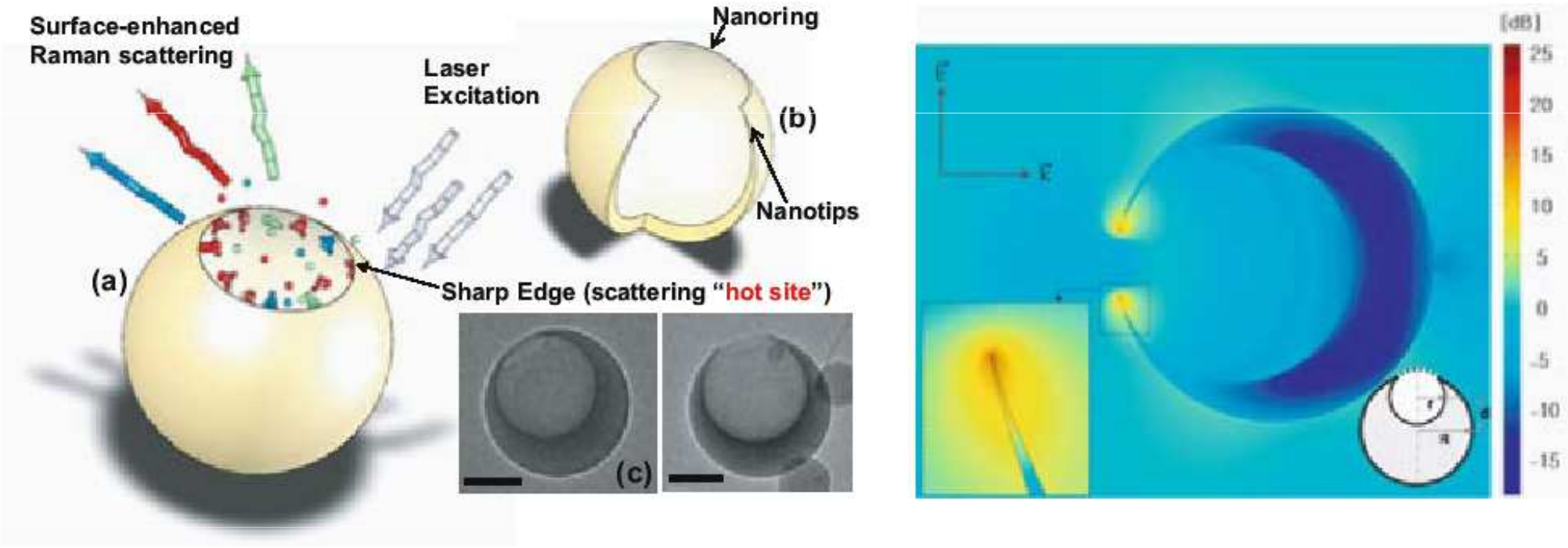




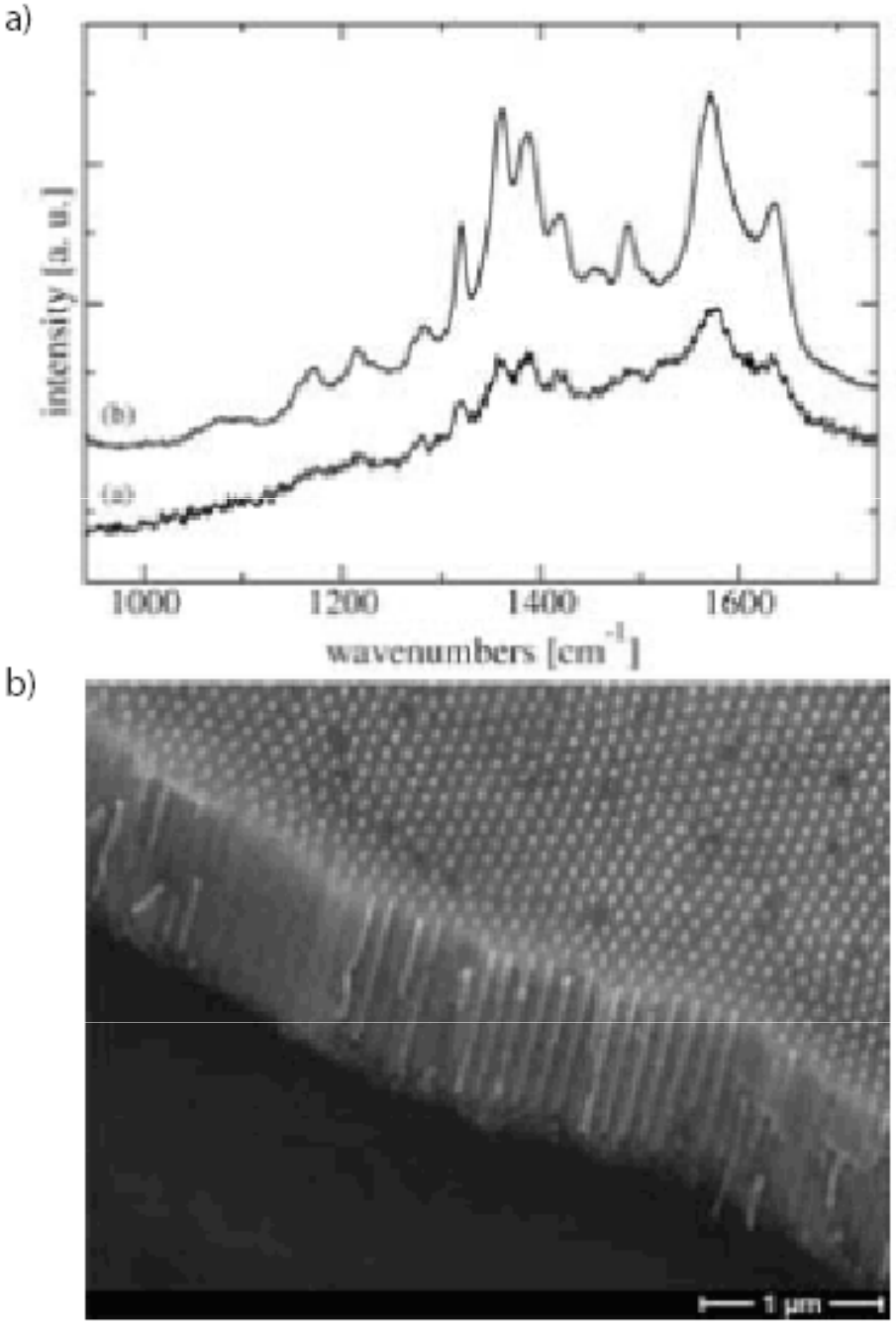
Spatial and spectral dependences of enhancement factors achieved at hot spots near the surface of array of silver nanospheres.



Schematics of SERS enhancement at hot spots in the array of nano-voids.



Schematics of SERS enhancement in metal crescent moon structure (left) and electric field distribution (right) showing hot-spots at the tips of the moon structure.



SERS spectra (a) and SEM image (b) of a gold nanowire array in a porous alumina matrix. Hot spots exist at the tips of the nanowires.

Conclusion:

1. The excitation of SPR causes the generation of the strong EM field near the surface of the nanoparticles. The optical processes in quantum system (molecules, nanoparticles, clusters, etc.) located in such plasmonic field are strongly enhanced.
2. The enhancement factor depends strongly on the size of metal nanoparticles and the gap between the nanoparticle and molecule. The maximal enhancement is achieved at size of 10 nm and gap of 10-30 nm.
3. The highest local field enhancement is achieved in the metal nanostructures with morphological features of few nanometers size providing the high gradient plasmonic field (so called “hot spots”).

THANK YOU
FOR ATTENTION !