Design and evaluation of cascaded plasmonic metamaterials

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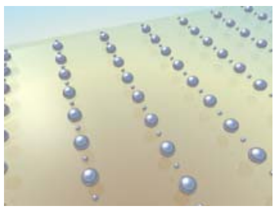
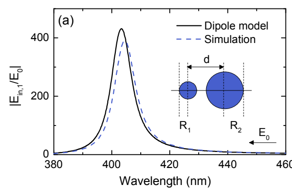
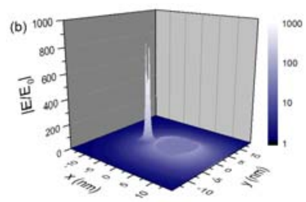
Calculations and simulations: Seyfollah Toroghi



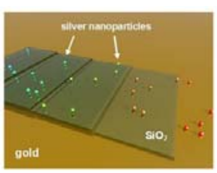


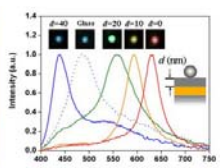


ARO MURI *Engineered Multifunctional Nanophotonic Materials for Ultrafast Optical Switching*

Plasmon enhanced nanophotonics

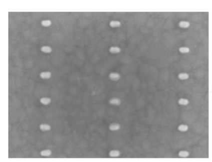
Dielectric control of Ag NP resonances

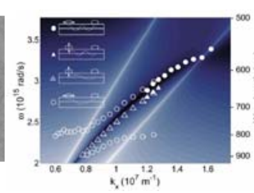




Hu et al. J. Phys. Chem. C 114, 7509 (2010)

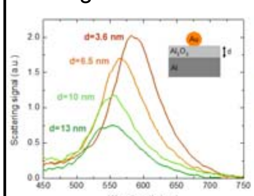
Hybrid plasmonic systems (LSP + SPP)

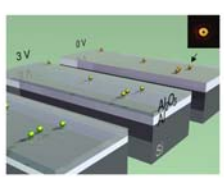




Ghoshal et al., Appl. Phys. Lett. 94, 171108 (2009)

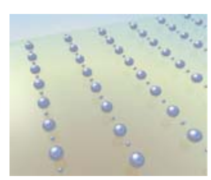
Voltage control of Au SP **Tue 9.40am 6B**

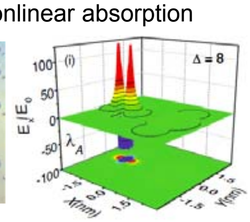




Lumdee et al., ACS Nano **6**, 6301 (2012)

LSP enhanced nonlinear absorption





Toroghi et al, PRB 85, 045432 (2012)

Outline

1. Introduction: Nonlinear optical absorption and refraction

   Plasmon resonant structures: approaches

2. Plasmon mediated electric field enhancement on spheres

   Cascaded localized plasmons on coupled spheres

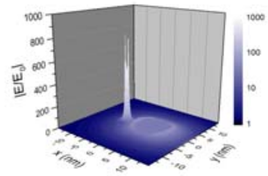
3. Nonlinear metamaterials using dissimilar nanospheres

   Enhanced nonlinear absorption using cascaded LSPs

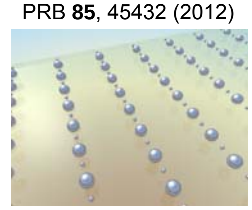
4. Fabrication challenges: spherical vs. shape-optimized

   Cascaded field enhancement in 2D compatible antennas

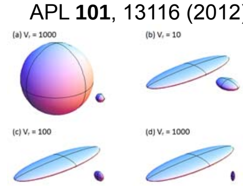
APL **100**, 183105 (2012)



PRB **85**, 45432 (2012)



APL **101**, 13116 (2012)



Nonlinear refraction and absorption

Applications of nonlinear refractive and absorptive materials

- Nonlinear transmission (e.g. sensor protection)
- beam shaping, beam steering
- all-optical switching (refractive or absorptive, waveguides or normal incidence)
- 3D displays

Holy grail for absorptive switching: low threshold NL absorption in thin film

Challenge: <u>nonlinear optical response generally weak</u>

⇒ Extremely large irradiance needed to achieve any significant NL absorption

Question: Can plasmon resonances increase the nonlinear absorption <u>performance</u> of switching materials?

Nonlinear absorption for ultrafast switching

In absence of 2nd order effects, polarization given by $P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(3)} E^3 + \ldots$

A finite $\chi^{(3)}$ leads to (complex) change in n: **$n = n_0 + (\eta_2' + i\,\eta_2'')\ I$**

⇒ High irradiance can induce refraction or absorption

Requirements:

- Transparent at low power
- Linear response must be non-diffractive / low scattering (effective medium)
- Thermally stable (non-spherical particles not ideal)
- Angle independent NL response (effective medium needed, non diffractive)
- Phase matching? NL response at fundamental frequency → not an issue

Best performance: small linear absorption α, large nonlinear absorption β

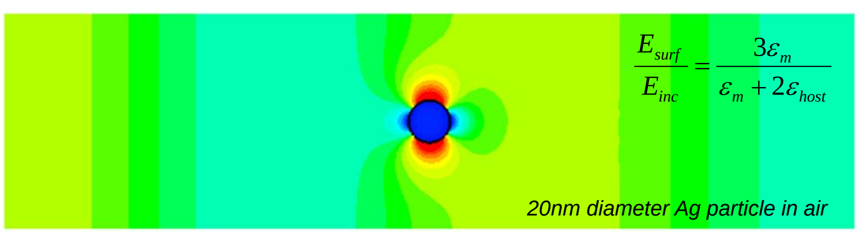
Enhancing local fields using surface plasmon resonance

Known: large field strength ⇒ large nonlinear response

Expect : field enhancement will modify local nonlinear optical polarization

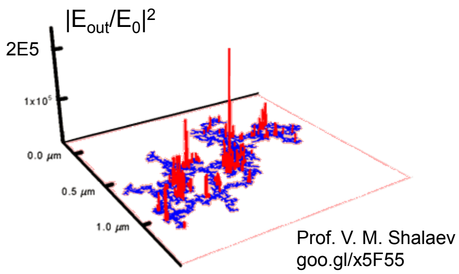
Questions:

- How does the localized surface plasmon resonance affect $\chi^{(3)}$ and n_2 ?
- How does the plasmon induced absorption affect the performance?
- Can we do better then individual spherical nanoparticles?



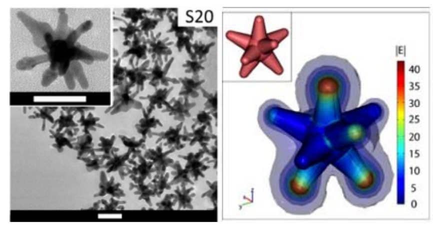
Nanostructures for plasmon enhanced fields

Fractals of silver nanoparticles



Prof. V. M. Shalaev
goo.gl/x5F55

Shaped particles, gold nanostars



Prof. Tuan Vo-Dinh
goo.gl/Diile

Large field enhancement (~500x)
Confined in few hot-spots
Spaced far apart (> λ)
Not effective medium ⇒ scatterer

Large enhancement ('lightning rod')
Several hot spots per NP, spacing < λ
Effective medium possible
Thermally unstable (reshape at high **I**)

Possible solution: **self-similar chain of nanoparticles** ('the world's smallest fractal')

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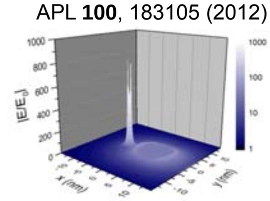
APL **100**, 183105 (2012)



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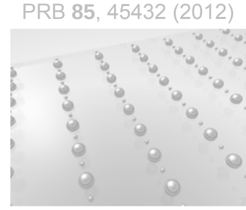
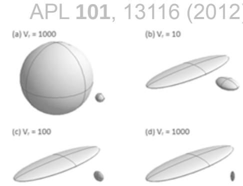


APL **101**, 13116 (2012)



Cascaded plasmon resonance

Isolated spherical plasmon resonant nanoparticles: known field enhancement

Fixed incident field strength E_0 $\Rightarrow$ enhanced field inside and outside NP at λ_{LSP}

Internal: $$g_{in} = \frac{E_{in}}{E_0} = \frac{3\,\varepsilon_h}{\varepsilon_m + 2\varepsilon_h}$$

External: $$g_{out} = \frac{E_{in}}{E_0} = \frac{3\,\varepsilon_m}{\varepsilon_m + 2\varepsilon_h}$$ (at surface)

[quasi-electrostatic limit / local dielectric function / negligible radiation loss]

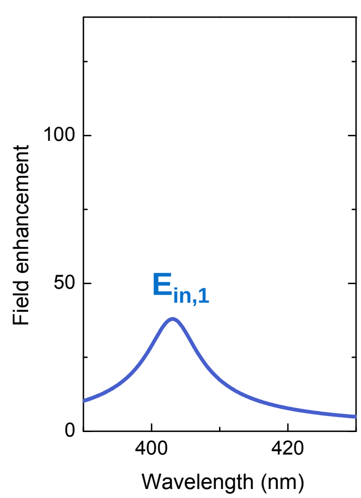
In polymeric hosts, typically $\varepsilon_h \approx 2.25 \Rightarrow \varepsilon_m' = -4.5 \Rightarrow g_{in} \approx 13.5 / Im[\varepsilon_m]$

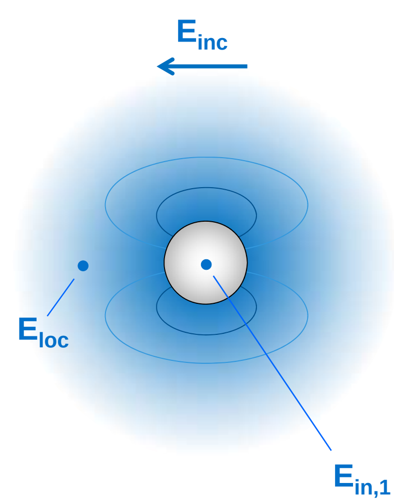
$\Rightarrow$ Noble metals, maximum external field enhancements in polymer of 10-50 $\times$

Further enhancement? ~~shaping~~ / ~~extended resonators~~ / coupled nanoresonators

Fields around isolated sphere

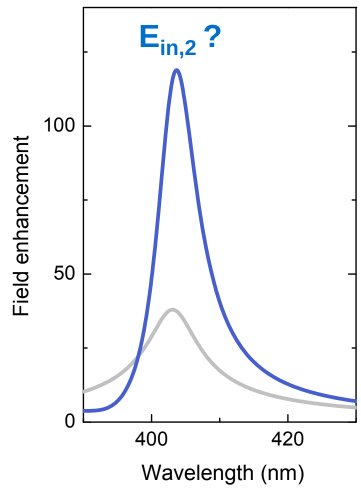
Isolated Ag nanoparticle (∅ = 10nm) – Internal and external field enhancement

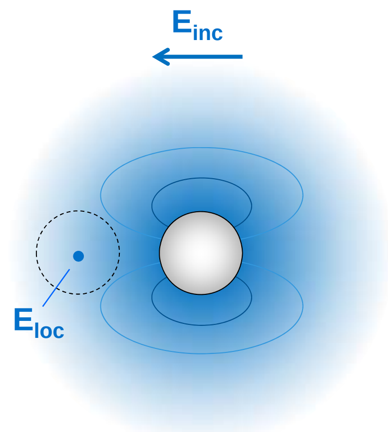




Predicted field in indirectly excited localized surface plasmon

Stronger field near particle surface (10nm distance) ⇒ can drive another NP



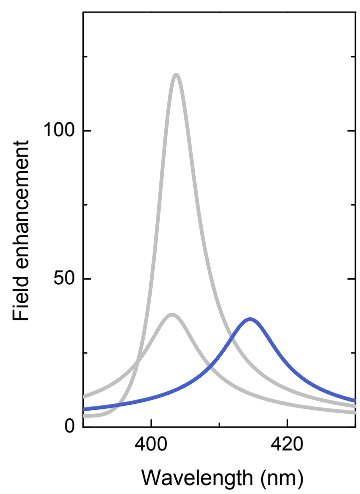


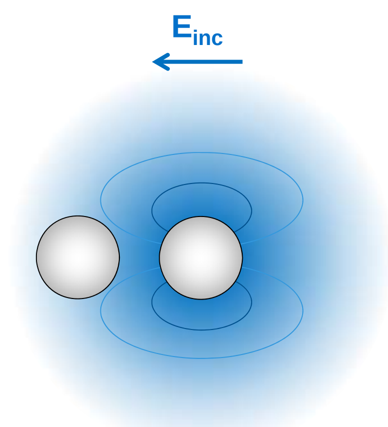
Multiply (E_{loc} / E_0) and single NP response?

We would call this '**multiplicative cascading**'

Detrimental effect of strong mutual interaction ('hindering')

Presence of second particle at 5nm edge-to-edge distance : mutual interaction



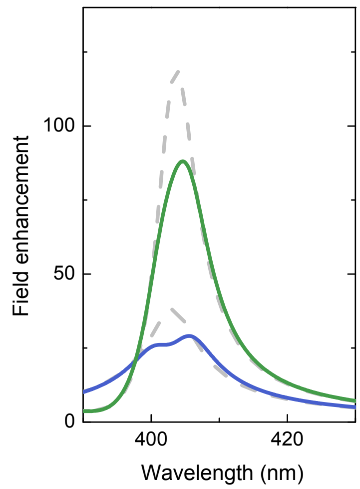


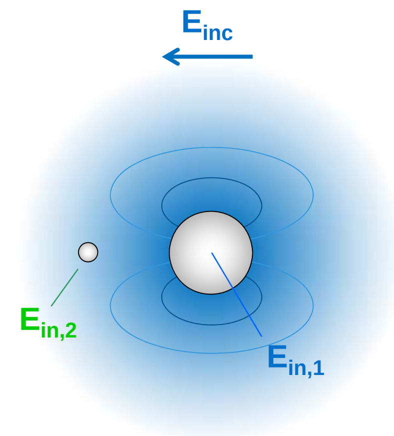
Strong interaction ⇒ resonance shifts

Observe (severely) '**hindered cascading**'

Near-multiplicative cascading at large size difference

Reduce volume of second particle ⇒ NP2 has only limited effect on NP1





Moderate mutual interaction ⇒

Cascaded field enhancement (hindered)

Effect of spacing on cascading

Bringing satellite particle closer ⇒ stronger fields, and more 'hindering'

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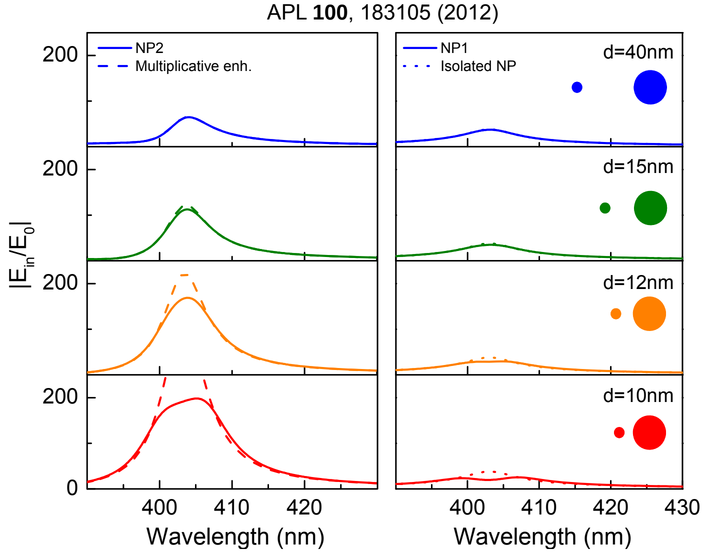


Ultimate limit?

Ultimate cascading limit - concept

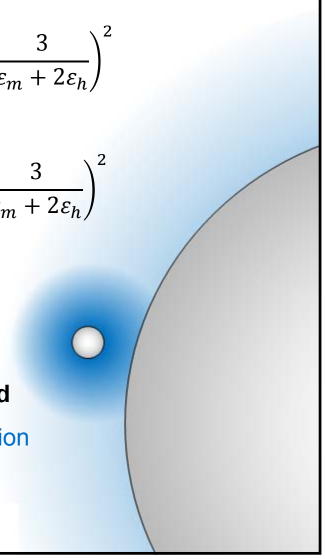
What would be the '**ultimate cascading limit**' for external field enhancement ?

Assume: make NP2 'infinitely' small, bring '**very**' close to surface of NP1

Max. external field: $$g_{ucl,in} = g_{out,1} \times g_{out,2} = \varepsilon_m^2 \left(\frac{3}{\varepsilon_m + 2\varepsilon_h} \right)^2$$

Max internal field: $$g_{ucl,in} = g_{out,1} \times g_{in,2} = \varepsilon_m \varepsilon_h \left(\frac{3}{\varepsilon_m + 2\varepsilon_h} \right)^2$$

Spectral location : at the **dipolar plasmon resonance**



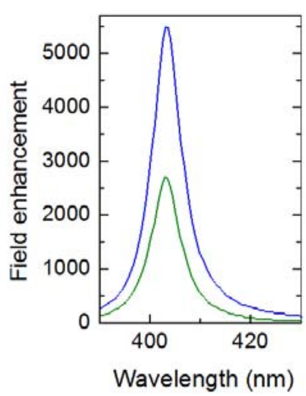
⇒ Cascading enables **large internal and external field**

Enhances host two-photon fluorescence, NL absorption

and metal nonlinear absorption and refraction

Ultimate cascading limit - magnitude

Calculated internal and external enhancement spectra



Field enhancement > 5000x

Predicted SERS enhancement ~10^{15}

Note: ratio $|g_{out}/g_{in}| = |\varepsilon_m / \varepsilon_h|$

At resonance: factor 2 (expected)

Does not include surface scattering / radiation loss / retardation / multipoles

Question: what kind of size differences and distances are needed?

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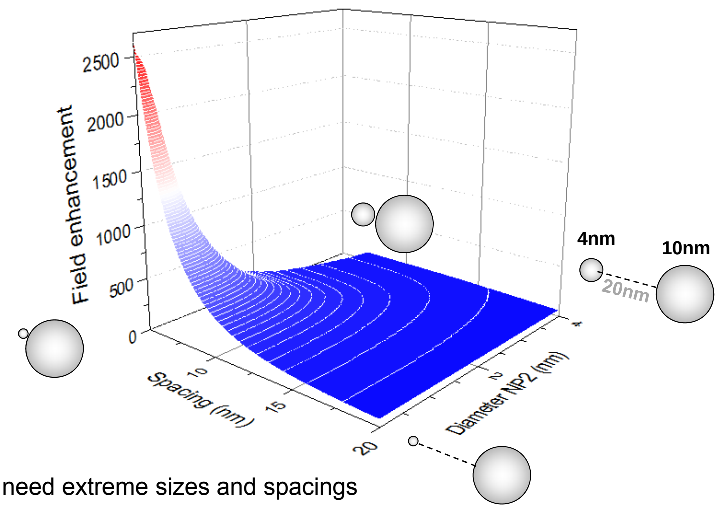
Ultimate cascading limit: size and spacing requirements

Calculated field enhancement vs. size and spacing for fixed ∅ NP1 =10nm



Note: need extreme sizes and spacings

Question: can we ignore radiation loss and multipoles?

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Full-field numerical simulation vs. point dipole model

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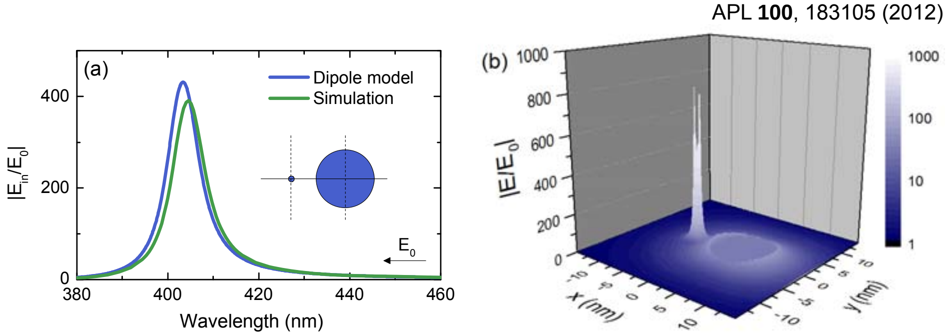

Example: Ag NP1 diameter 10 nm, NP2 diameter 1nm, spacing 9 nm

Compare dipole coupling model and full 3D numerical simulation
⇒ good agreement, significant cascading

Goal: utilize cascaded enhancement in nonlinear metamaterial

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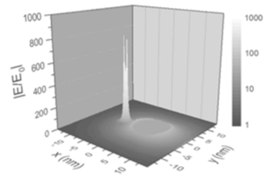

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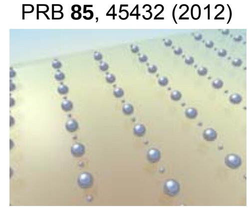
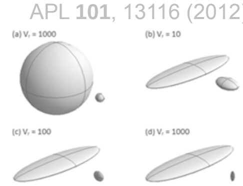
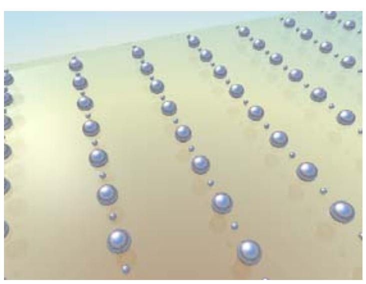


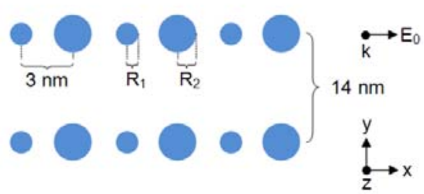
APL **101**, 13116 (2012)



Cascaded plasmon resonant nonlinear metamaterials



"Artist's" rendering of cascaded NL metamaterial



Systematic study of the effect of cascading on NLO switching:

- Choose fixed metal fill fraction (3%)
- Five structures, stepwise increase of size difference

This talk: Leverage nonlinear response of metal (host response also increases)

NL susceptibility enhancement factor in dense structures

Composite NL susceptibility can be written in terms of enhancement factors g:

$$\chi_c^{(3)} = f_{in} g_{in}^{(3)} \chi_{in}^{(3)} + f_h g_h^{(3)} \chi_h^{(3)}$$

Here: note fraction not included in enhancement factor.

Dense arrays: no simple analytical formulas (near-field coupling, multipoles)

For known simulated linear field distribution, enhancement factors given by :

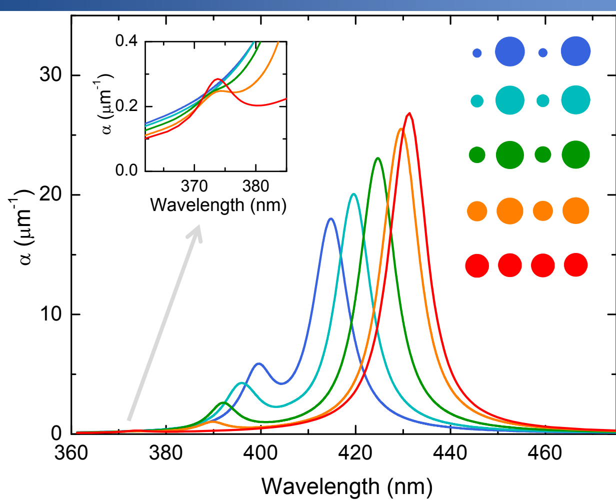
$$g_j^{(3)} = \frac{\left\langle \vec{E}^2 \left|\vec{E}\right|^2 \right\rangle_{V_j}}{\left\langle \vec{E} \right\rangle_V^2 \left|\left\langle \vec{E} \right\rangle_V\right|^2}$$

V_j = volume of inclusion or of host (j=in or h)

V = volume of unit cell

These represent *enhancement of $\chi^{(3)}$ contribution from host or inclusion, relative to the expected value based on a homogeneous E distribution*

Effect of cascading on linear absorption

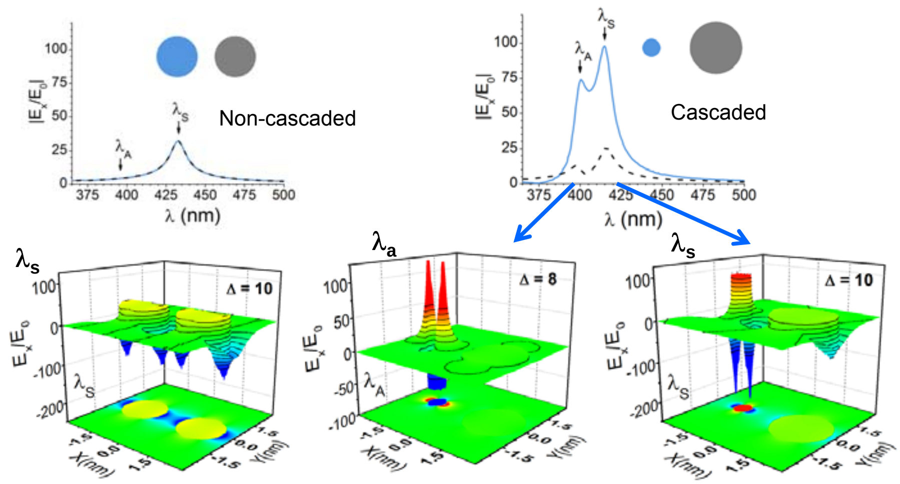


No size difference: one main absorption, small multipole peak

Large size difference: additional resonance feature present

Nature of resonances follows from field distribution at key frequencies

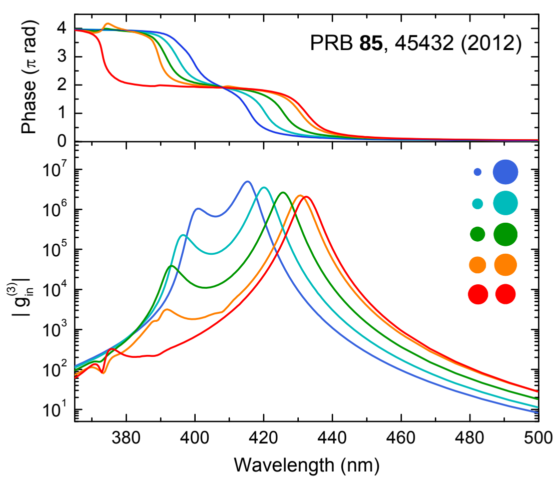
Cascaded field enhancement



Cascaded structure: larger internal enhancement, new anti-symmetric mode

Question: how does cascading affect NL enhancement factors

Complex enhancement of metal nonlinear response

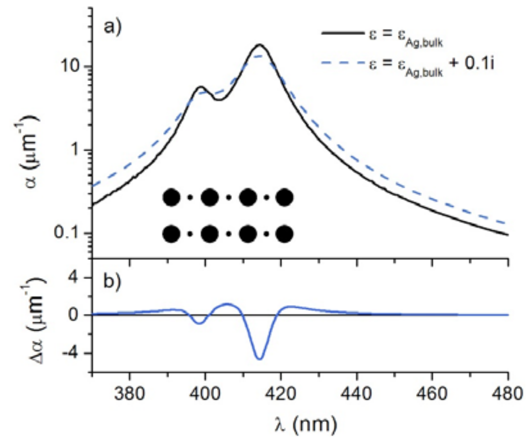


Complex enhancement of $\chi^{(3)}$ now shows **two main resonances**

Enhancement of antisymmetric mode increases as size difference is increased

Phase of enhancement at peaks : π. **New**: phase of between resonances: 0 π

Understanding the complex enhancement factor



Increased damping leads to broadened resonances

At frequencies between modes, this results in an increased absorption

Magnitude of this effect is amplified by cascaded field enhancement

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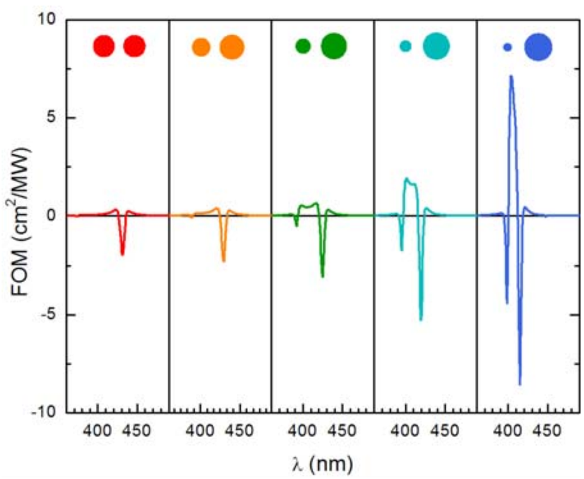
Figure of merit for nonlinear absorption



Example: assuming $Im(\chi_{Ag}^{(3)}) = 10^{-16}$ m^2/V^2 calculate β/α vs. cascading

Result: dramatically improved response compared to single particle size

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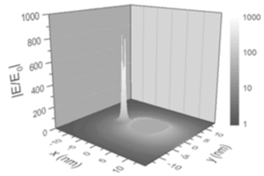

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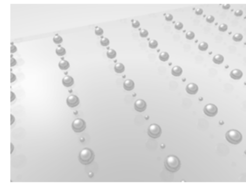

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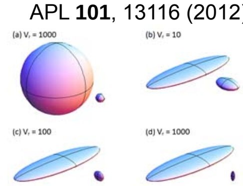


4. Fabrication challenges: spherical vs. shape-optimized

   Cascaded field enhancement in 2D compatible antennas

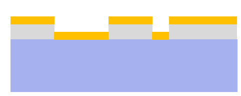
Challenge – large area fabrication of cascaded nanoantennas

Thus far: nanospheres with large volume difference ⇒ large field enhancement

Ideal for high power image-preserving optical absorbing layers

- non-scattering (many closely spaced identical elements)
- spherical elements (surface melting ⇒ limited reshaping)
- large field enhancement factors, NLO response

Challenge: Not compatible with 2D fabrication?



Appears to be intrinsic problem: cascading requires

- Difference in volume to reduce 'hindering' (back action)
- Identical resonance frequency needed for coupling

⇒ Can only use particles with identical aspect ratio, making this 2D incompatible?

Approach: shape optimization

Challenge: keep thickness fixed, modify volume without changing λ_{LSP}

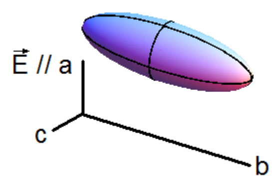
Approach: 'in-plane' shape optimization. First approach: use ellipsoids

Field enhancement: $$\frac{E_{in}}{E_0} = \frac{\varepsilon_h}{\varepsilon_h + L_a(\varepsilon_m - \varepsilon_h)}$$

Dipolar resonance when $\varepsilon_m = -(1/L_a - 1)\,\varepsilon_h \equiv -R\ \varepsilon_h$ (sphere: R = 2)

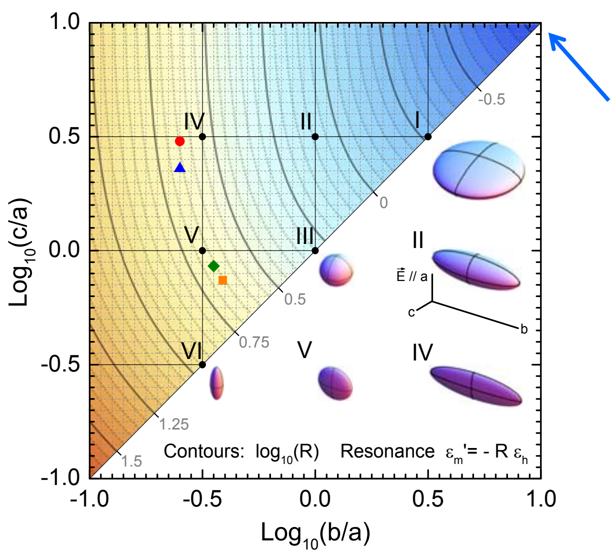
Shape factor L_a for ellipsoid with axis lengths a, b, c :

$$L_a = \frac{abc}{2}\int_0^\infty (a^2+q)^{-\frac{3}{2}}(b^2+q)^{-\frac{1}{2}}(c^2+q)^{-\frac{1}{2}}\,dq$$



Question: can we vary the shape while maintaining λ_{LSP}?

Effect of particle shape on resonance condition



Examples

Flat disk: $R = 10^{-0.75} = 0.2$

Resonance $\varepsilon_m = -0.2\ \varepsilon_h$

Close to ω_p

Sphere: $R = 10^{0.3} = 2$

Resonance $\varepsilon = -2\ \varepsilon_h$

Note: isolines present

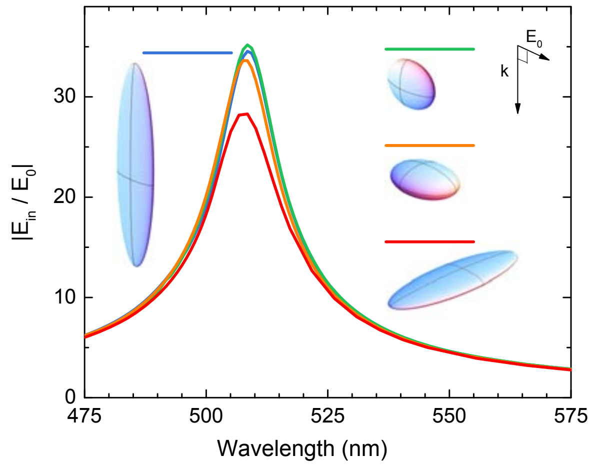
$\Rightarrow$ **Different shape, Same λ_{LSP}**

Next: Consider shapes indicated by colored symbols

APL **101**, 13116 (2012)

Field enhancement in shape optimized ellipsoids

Numerical simulation of internal field enhancement in four shape tuned ellipsoids



Shapes with axes (a,b,c)

2.2 nm, 0.58 nm, **5 nm**

5.8 nm, 2.1 nm, **5 nm**

12.8 nm, **5 nm**, 9.4 nm

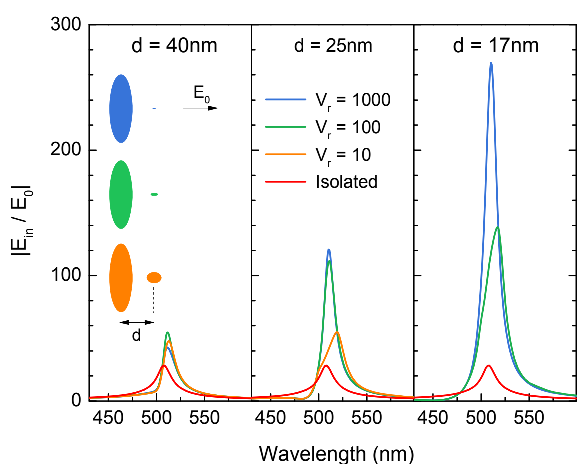
20 nm, **5 nm**, 60 nm

APL **101**, 13116 (2012)

Success: different shape, same resonance frequency.. Retardation affects E_{max}

Cascaded field enhancement in shape tuned ellipsoid dimers

Combination of largest particle with either of the three smaller shapes



Left: large spacing
No hindering observed
Small enhancement

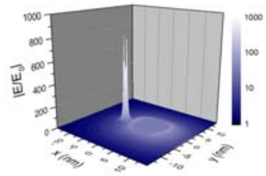
Middle: medium spacing
Hindering for large NP,
Increased enhancement

Right: small spacing
Smallest NP: multiplicative,
Large enhancement

Success: significant cascading in shape optimized 2D compatible dimer antennas

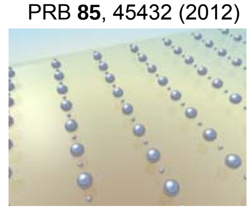
Conclusions

APL **100**, 183105 (2012)



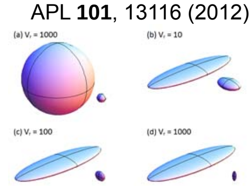
- Ideal cascaded plasmon resonance can produce field enhancement > 1000 in simple NP dimer
- Relatively large volume ratios needed (> 100)

PRB **85**, 45432 (2012)



- Assembling cascaded dimers into metamaterial
  $\Rightarrow$ dramatically enhanced NLO absorption and refraction
- Cascaded structures outperform non-cascaded structures
- Spherical shapes : thermally stable

APL **101**, 13116 (2012)



- Nanosphere cascading incompatible with 2D nanofab
- Shape cascading : in-plane shape optimized resonance
- Better for low power applications (SERS, biosensing)