Design and evaluation of cascaded plasmonic metamaterials

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ARO MURI  Engineered Multifunctional Nanophotonic Materials for Ultrafast Optical Switching

Plasmon enhanced nanophotonics

Dielectric control of Ag NP resonances  Hybrid plasmonic systems (LSP + SPP)


Voltage control of Au SP  LSP enhanced nonlinear absorption

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

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: nonlinear optical response generally weak
⇒ Extremely large irradiance needed to achieve any significant NL absorption

Question: Can plasmon resonances increase the nonlinear absorption performance of switching materials?
Nonlinear absorption for ultrafast switching

In absence of 2nd order effects, polarization given by

\[ P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(3)} E^3 + ... \]

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 \( \alpha \), large nonlinear absorption \( \beta \)

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 than individual spherical nanoparticles?

\[ \frac{E_{\text{surf}}}{E_{\text{inc}}} = \frac{3 \varepsilon_m}{\varepsilon_m + 2 \varepsilon_{\text{host}}} \]

20nm diameter Ag particle in air
Nanostructures for plasmon enhanced fields

Fractals of silver nanoparticles

Shaped particles, gold nanostars

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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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 \( \lambda_{LSP} \)

Internal:
\[
g_{\text{in}} = \frac{E_{\text{in}}}{E_0} = \frac{3\,\varepsilon_h}{\varepsilon_m + 2\varepsilon_n}
\]

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

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

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

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

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

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**Fields around isolated sphere**

Isolated Ag nanoparticle (\( \varnothing = 10\text{nm} \)) – Internal and external field enhancement

![Fields around isolated sphere](image)

\( E_{\text{inc}} \)

\( E_{\text{loc}} \)

\( E_{\text{in,1}} \)

\( E_{\text{in,2}} \)
Predicted field in indirectly excited localized surface plasmon

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

\[ E_{\text{inc}} \]

Multiply \( \left( \frac{E_{\text{loc}}}{E_0} \right) \) 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

\[ E_{\text{inc}} \]

Strong interaction ⇒ resonance shifts

Observe (severely) ‘**hindered cascading**’
Near-multiplicative cascading at large size difference

Reduce volume of second particle \(\Rightarrow\) NP2 has only limited effect on NP1

Moderate mutual interaction \(\Rightarrow\) Cascaded field enhancement (hindered)

Effect of spacing on cascading

Bringing satellite particle closer \(\Rightarrow\) stronger fields, and more ‘hindering’

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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:  \[ g_{out,1} \times g_{out,2} = \varepsilon_m^2 \left( \frac{3}{\varepsilon_m + 2\varepsilon_h} \right)^2 \]

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

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

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Ultimate cascading limit - magnitude

Calculated internal and external enhancement spectra

Field enhancement > 5000x

Predicted SERS enhancement \( \sim 10^{15} \)

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?
Ultimate cascading limit: size and spacing requirements

Calculated field enhancement vs. size and spacing for fixed \( \text{NP}_1 = 10 \text{nm} \)

Note: need extreme sizes and spacings

Question: can we ignore radiation loss and multipoles?

Full-field numerical simulation vs. point dipole model

Example: Ag \( \text{NP}_1 \) diameter 10 nm, \( \text{NP}_2 \) diameter 1 nm, spacing 9 nm

Compare dipole coupling model and full 3D numerical simulation

\( \Rightarrow \) good agreement, significant cascading

Goal: utilize cascaded enhancement in nonlinear metamaterial
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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)
Composite NL susceptibility can be written in terms of enhancement factors $g$:

$$\chi_c^{(3)} = \int \chi_{in}^{(3)} + f_h \chi_h^{(3)}$$

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:

$$g_j^{(3)} = \frac{\langle \hat{E}_j^2 \rangle_{V_j}}{\langle \hat{E}^2 \rangle_{V_j}}$$

$V_j = \text{volume of inclusion or of host (j=\text{in} or h)}$

$V = \text{volume of unit cell}$

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: $\pi$.

**New:** phase of between resonances: $0 \pi$
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.

**Figure of merit for nonlinear absorption**

**Example:** assuming \(\text{Im}(\chi_{Ag}^{(3)}) = 10^{-16} \text{m}^2/\text{V}^2\) calculate \(\beta/\alpha\) vs. cascading

**Result:** dramatically improved response compared to single particle size.
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Challenge – large area fabrication of cascaded nanoantennas

**Thus far:** nanospheres with large volume difference \(\Rightarrow\) large field enhancement

Ideal for high power image-preserving optical absorbing layers
- non-scattering (many closely spaced identical elements)
- spherical elements (surface melting \(\Rightarrow\) 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

\(\Rightarrow\) Can only use particles with identical aspect ratio, making this 2D incompatible?
**Approach: shape optimization**

**Challenge:** keep thickness fixed, modify volume without changing $\lambda_{LSP}$

**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 $a, b, c$:

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

**Question:** can we vary the shape while maintaining $\lambda_{LSP}$?

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**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 $\omega_p$

- Sphere: $R = 10^{0.3} = 2$
- Resonance $\varepsilon = -2 \varepsilon_h$

Note: isolines present

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

**Next:** Consider shapes indicated by colored symbols

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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

*Success:* different shape, same resonance frequency. Retardation affects $E_{\text{max}}$

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

- Ideal cascaded plasmon resonance can produce field enhancement > 1000 in simple NP dimer
- Relatively large volume ratios needed (> 100)
- Assembling cascaded dimers into metamaterial ⇒ dramatically enhanced NLO absorption and refraction
- Cascaded structures outperform non-cascaded structures
- Spherical shapes: thermally stable
- Nanosphere cascading incompatible with 2D nanofab
- Shape cascading: in-plane shape optimized resonance
- Better for low power applications (SERS, biosensing)