Enhanced Nonlinear Optical Response from Nano- and Micro-Scale Composite Materials

Robert W. Boyd
The Institute of Optics, University of Rochester, Rochester, NY 14627, USA

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The Promise of Nonlinear Optics

Nonlinear optical techniques hold great promise for applications including:

• Photonic Devices
• Quantum Imaging
• Quantum Computing/Communications
• Optical Switching
• Optical Power Limiters
• All-Optical Image Processing

But the lack of high-quality photonic material is often the chief limitation in implementing these ideas.
Composite Materials for Nonlinear Optics

Want large nonlinear response for applications in photonics

One specific goal:
   Composite with $\chi^{(3)}$ exceeding those of constituents

Approaches:

- Nanocomposite materials
  Distance scale of mixing $<< \lambda$
  Enhanced NL response by local field effects

- Microcomposite materials (photonic crystals, etc.)
  Distance scale of mixing $\approx \lambda$
  Constructive interference increase E and NL response
Material Systems for Composite NLO Materials

All-dielectric composite materials
- Minimum loss, but limited NL response

Metal-dielectric composite materials
- Larger loss, but larger NL response
- Note that $\chi^{(3)}$ of gold $\approx 10^6$ $\chi^{(3)}$ of silica glass!
- Also, metal-dielectric composites possess surface plasmon resonances, which can further enhance the NL response.
Nanocomposite Materials for Nonlinear Optics

- Maxwell Garnett
- Bruggeman (interdispersed)
- Fractal Structure
- Layered

scale size of inhomogeneity $\ll$ optical wavelength
Gold-Doped Glass: A Maxwell-Garnett Composite

- Red color is because the material absorbs very strongly in the blue, at the surface plasmon frequency
- Composite materials can possess properties very different from those of their constituents.
- Red Glass Caraffe Nuremberg, ca. 1700
  Huelsmann Museum, Bielefeld

Developmental Glass, Corning Inc.

gold volume fraction approximately $10^{-6}$
gold particles approximately 10 nm diameter
Demonstration of Enhanced NLO Response

- Alternating layers of TiO$_2$ and the conjugated polymer PBZT.
- Measure NL phase shift as a function of angle of incidence.

\[ \nabla \cdot \mathbf{D} = 0 \] implies that \((\varepsilon \mathbf{E})_\perp\) is continuous.

Thus field is concentrated in lower index material.

Enhanced EO Response of Layered Composite Materials

\[ \chi_{ijkl}^{(\text{eff})}(\omega';\omega,\Omega_1,\Omega_2) = f_a \left[ \frac{\varepsilon_{\text{eff}}(\omega')}{\varepsilon_a(\omega')} \right] \left[ \frac{\varepsilon_{\text{eff}}(\omega)}{\varepsilon_a(\omega)} \right] \left[ \frac{\varepsilon_{\text{eff}}(\Omega_1)}{\varepsilon_a(\Omega_1)} \right] \left[ \frac{\varepsilon_{\text{eff}}(\Omega_2)}{\varepsilon_a(\Omega_2)} \right] \chi_{ijkl}^{(a)}(\omega';\omega,\Omega_1,\Omega_2) \]

- AF-30 (10%) in polycarbonate (spin coated)
  \( n=1.58 \quad \varepsilon(\text{dc}) = 2.9 \)
- barium titante (rf sputtered)
  \( n=1.98 \quad \varepsilon(\text{dc}) = 15 \)

\[ \chi_{zzzz}^{(3)} = (3.2 + 0.2i) \times 10^{-21} (m / V)^2 \pm 25\% \]

\[ \approx 3.2 \chi_{zzzz}^{(3)} (\text{AF-30 / polycarbonate}) \]

3.2 times enhancement in agreement with theory

Metal / Dielectric Composites

Very large local field effects

\[ E_{in} = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} E_0 = \lambda E_0 \]

(\(\varepsilon_m\) is negative!)

At resonance

\[ \lambda = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} \rightarrow \frac{3\varepsilon_h}{i\varepsilon_m''} \approx (3 \text{ to } 30) i \]

\[ \chi_{eff}^{(3)} = f \left| Z \right|^2 \chi_m^{(3)} + (1-f) \chi_h^{(3)} \]
Counter-intuitive Consequence of Local Field Effects

gold nanoparticles in a liquid dye solution (HITCl)

Both constituents are reverse saturable absorbers \( \Rightarrow \text{Im } \chi^{(3)} > 0 \)

Effective NL susceptibility of composite

\[
\chi^{(3)}_{\text{eff}} = f \chi_{\text{Au}}^{(3)} + (1-f) \chi_{\text{dye soln}}^{(3)}
\]

\[
z = \frac{3E_h}{E_m + 2E_h} = \text{pure imaginary at resonance!}
\]

A cancellation of the two contributions to \( \chi^{(3)} \) can occur, even though they have same sign.

Smith et al., JOSA B 14 1625 1997.
Counterintuitive Consequence of Local Field Effects

Cancellation of two contributions that have the same sign

Gold nanoparticles in a saturable absorber dye solution (13 μM HITCI)

\[ \chi_{\text{eff}}^{(3)} = f |L|^2 L^2 \chi_i^{(3)} + \chi_h^{(3)} \]

Comparison of Bulk and Colloidal Gold

Open Aperture Z-Scans of Gold Colloid and Au film at 532nm

- Nonlinearities possess opposite sign!
Nonlinear Optical Response of Semicontinuous Metal Films

Measure nonlinear response as function of gold fill fraction

![Graph showing nonlinear absorption $\beta$ (cm/W) vs. fill fraction with percolation threshold marked near 0.4 and MG theory (D=2.38) line]

(with D. D. Smith and G. Piredda)
Artificial Materials for Nonlinear Optics

Artificial materials can produce
Large nonlinear optical response
Large dispersive effects

Examples
- Fiber/waveguide Bragg gratings
- PBG materials
- CROW devices (Yariv et al.)
- SCISSOR devices
Third-Harmonic Generation in a 3D Photonic Crystal

Polystyrene photonic crystal

Direct THG visible by eye!

Phase matching provided by PBG structure.

• Metals have very large optical nonlinearities but low transmission

• Low transmission is because metals are highly reflecting (not because they are absorbing!)

• Solution: construct metal-dielectric photonic crystal structure (linear properties studied earlier by Bloemer and Scalora)

Greater than 10 times enhancement of NLO response is predicted!

“Loss” mechanisms in copper

Intraband (d-p) absorption

Drude reflection region

Cu

\[ \lambda, \text{nm} \]

[k", \varepsilon""]
Accessing the Optical Nonlinearity of Metals with Metal-Dielectric Photonic Crystal Structures

- Metal-dielectric structures can have high transmission.
- And produce enhanced nonlinear phase shifts!

The imaginary part of $\chi^{(3)}$ produces a nonlinear phase shift!
(And the real part of $\chi^{(3)}$ leads to nonlinear transmission!)
Linear Transmittance of Samples

Material (interband) feature

Structural (M/D PC) feature

Cu: 40 nm film

M/D PC: Cu / silica

5x16/98 nm (80 nm total Cu)
Mechanism of nonlinear response: “Fermi smearing”

\[ \Delta T \rightarrow \Delta \varepsilon (E_{IB}) \rightarrow \text{change in optical properties} \]

Near the interband absorption edge, “Fermi smearing” is the dominant nonlinear process

\[ \chi^{(3)} \text{ is largely imaginary} \]

Reflection/Transmission Z-Scan

Pulse energy $\sim 1 \text{m J}$
$I = 100 \text{MW/cm}^2$

$\frac{\Delta R}{R}, \frac{\Delta T}{T} \rightarrow \Delta \varepsilon' + \Delta \varepsilon''$
Z-Scan Comparison of M/D PC and Bulk Sample

- We observe a large NL change in transmission
- But there is no measurable NL phase shift for either sample

Nonlinear Transmission and Reflectance

Material (interband) feature

Structural (M/D PC) feature

\[ \Delta T/T \] (M/D PC)

\[ \Delta R/R \] (M/D PC)

\[ \Delta T/T \] (bulk)

\[ -\Delta T/T, -\Delta R/R \]

wavelength, nm

560  600  640  680
Nonlinear phase shift of PC (numerical simulations)

\[ \Delta \varepsilon = 0.1i \rightarrow \Delta n \]

- Appreciable \( \Delta n \) occurs only outside of transparency window
- Next step: design and fabricate new structure
Conclusions

• Both nano-scale and microscale structuring can lead to enhanced nonlinear optical effects

• Influence of nano-scale structuring can be understood in terms of local field effects

• Nano-scale structuring can lead to enhancement (layered results) or cancellation (dye/colloid) of NLO response

• Influence of microscale structuring can be understood in terms of properties of photonic crystals

• Dispersion induced by photonic crystal can lead to new phase-matching effects

• Metal / dielectric photonic crystals can be designed to allow access to the large nonlinearity of metals
Special Thanks to My Students and Research Associates
Thank you for your attention!
Approaches to the Development of Improved NLO Materials

• New chemical compounds
• Quantum coherence (EIT, etc.)
• Composite Materials:
  (a) Microstructured Materials, e.g. Photonic Bandgap Materials, Quasi-Phasematched Materials, etc
  (b) Nanocomposite Materials

These approaches are not incompatible and in fact can be exploited synergistically!