3D Active Photonic Nanostructures

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Direct fs Laser Writing

- DLW - a technology that allows the 3D structuring of photopolymers
- By employing nonlinear absorption, it’s possible to bypass Beer’s law
- By employing materials with polymerization threshold, it’s possible to overcome the diffraction limit

Applications of DLW

Micro-optics

Models

3D scaffolds for cell cultures

Biomedical Implants
Active Photonic Nanostructures

• Main Challenges: Resolution, Functionality

High Resolution Quantum Dot and Metallic Nanostructures
Active Photostructurable Materials

- Majority of applications involve commercially-available negative photo-resists such as SU8.
- Good structural results but limited flexibility when it comes to bulk or surface functionalization.
- **Sol-gel Chemistry**: a chemical process for the incorporation of inorganic compounds into organic molecules,
- Photosensitive sol-gels undergo through two polymerizations, inorganic and organic—possible elimination of shrinkage
- Easily functionalized, surface and bulk

We research materials containing quantum dots and metal-binding materials
Problem
Unlike electrons, photons cannot be easily dynamically tuned.

Solution
Nonlinear Photonic Crystals—structures whose optical response depends on the intensity of the optical field that propagates in them.

2PP Solution
3D structures fabricated using nonlinear optical materials.
Disadvantages

- Electrical Poling required
- Low nonlinearity
- Degradation

Quantum-Dot materials

- Quantum dots (QDs) are well known for their large third-order non-linearity
- QDs have to be part of the photopolymer, otherwise they wash out during structure development
- Existing materials are acrylates and QD-doped ORMOCER—not high enough resolution for photonic applications.
- We choose *in situ* synthesis of CdS QDs, to avoid absorption and scattering due to aggregation.

Hybrid materials synthesized via the Sol-Gel process

**Organic monomers**

- Dimethylaminoethyl methacrylate (DMAEMA)
- Methacrylic acid
- Methacryloxypropyltrimethoxy silane (MAPTMS)

**Metal alkoxides**

**Photoinitiator**

- 4,4’ – Bis(diethylamino) benzophenone (BIS)
Quantum Dot Formation

$3D \text{ structure containing Cd QD precursors} + \text{Na}_2S = 3D \text{ structure containing CdS QDs}$

Before QD formation

After QD formation

Crystalite: 1.5 nm
(Debye-Scherrer formula)
QD: 3.6 nm
Material Properties

Fluorescence

3rd order nonlinearity (z-scan)
QD-containing structures
Woodpile structures with 1700 nm period
**Linear Optical Properties**

**Theoretical calculations**

- **Bandgap**
  - $a = 1.414 \times d$, $d = 850\text{nm}$, $a/\lambda \sim 0.86$: $\lambda = 2.79\mu\text{m}$
  - $a = 1.414 \times d$, $d = 1700\text{nm}$, $a/\lambda \sim 0.855$: $\lambda = 1.41\mu\text{m}$

**Right panel: FTIR spectrum**

- **FTIR measurements of photonic woodpile structures with period**
  - $d = 1700\text{nm}$, $\lambda = 2.67\mu\text{m}$: very good agreement between theoretical calculations ($2.79\mu\text{m}$) and experimental results
  - $d = 850\text{nm}$, $\lambda \sim 1.35\mu\text{m}$ (?): just in the edge of the measurement range of the spectrometer, though it’s very close to the theoretical calculation of $\lambda = 1.41\mu\text{m}$

We can also clearly see the absorption bands at $3.4\mu\text{m}$ and $3.0\mu\text{m}$ due to the material itself.
900nm-700nm period
600nm-500nm period
400nm period
What is a metamaterial?

- Metamaterial is an artificial material which electromagnetic properties ($\varepsilon$, $\mu$) can be controlled.
- It is made up of periodic arrays of metallic resonant elements.
- Both the size of the element and the unit cell are small relative to the wavelength.

Metamaterials can exhibit left-handed ($\mu > 0$, $\varepsilon < 0$) and right-handed ($\mu < 0$, $\varepsilon > 0$) behavior.

Metals at optical frequencies ($\mu < 0$, $\varepsilon < 0$) and isotropic dielectrics ($\mu > 0$, $\varepsilon > 0$) are also considered.

$\text{Size of element} \ll \lambda$

$d \ll \lambda$
How do you make a 3D metallic nanostructure?

Seeding

Photosensitive sol-gel +DMAEMA

Plating

Silver

Photosensitive sol-gel +DMAEMA
Conducting woodpiles

600 nm period

![Image of woodpile structure]

![Graph showing voltage and current relationship with different resistances]

Voltage (V) vs. Current (A) graph with markers for resistances 3.14, 3.24, 3.41, 3.45, 4.02, and 3.53 ohms.

15 kV, X90, 200 μm
Modeling and Characterization

α  Lattice constant (distance from center-to-center)

d  Period of the structure

R1  Small radius of ell. cylinder

R2  Big radius of ell. cylinder
Conclusions

- Synthesis of NLO material containing CdS quantum dots
- Fabrication of woodpile structures with period down to 400nm
- Fabrication of silver, conducting 3D structures with period 600 nm

Ongoing research

- Measurement of the bandgap shift due to nonlinearity
- Fabrication of NLO photonic crystals with periodicity < 400 nm with 1\textsuperscript{st} order bandgaps at visible wavelengths, near resonance.
- Novel designs for 3D metamaterials
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