Cristalli fotonici colloidali 3D e loro applicazioni nel campo della sensoristica.

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OUTLINE

- Introduction
- Fabrication methods
- Applications:
  - Strain sensor
  - SERS substrate
- Conclusions
**Introduction**

**All-Optical Micropolis**

“comunication of the data occurs using just all-optical device.”

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**Why Photonic Crystals?**

*Reduce the dimension of optical functions.*

*Increasing the density of the functions in the integrated circuits.*

“Joannopoulos’ vision”
3D Photonic Crystals

√ S. Y. Lin *Nature* 394, 251, (1998);

*Nanolithography*

√ M. Campbell *Nature* 404, 53, (2000);

*Holography*


*Direct Laser Writing*

These techniques are based on *highly expensive* and *sophisticated equipment*.
What are colloidal crystals?

3D Photonic Crystals

Self-Assembling colloidal nano-microspheres

Low cost
associated with their manufacture

“Easy”
relative easiness of preparation
The reaction takes place at room temperature and we can control the particle size through the concentration of a single reactive.

Molar Concentrations

- \([\text{TEOS}] = 0.22 \text{ M}\)
- \([\text{NH}_3] = 1.0 \text{ M}\)
- \([\text{H}_2\text{O}] = 15.0 \text{ M}\)

The dimension of silica spheres is approximately 255 nm.

Stober Methods

\[
\text{Si(OC}_2\text{H}_5\text{)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O}
\]

Silica Spheres

High uniformity of silica spheres (less than 5% of dispersion in diameter)
**PS monosize spheres**

**Single-stage polymerization process**

based on formation and growth of polymeric nuclei dispersed in an emulsion constituted by water, styrene, potassium persulfate (KPS) and sodium docecyl sulfate (SdS).

Range 150 ÷ ~ 1000 nm

**Control the particle size through the concentration of sodium docecyl sulfate.**
Techniques

Self Assembly techniques

Vertical Deposition

Properties of colloidal crystals

Exploit the property of NPs to self-assemble in ordered structure

The matrix is made of close-packed NPs arranged in a face-centered-cubic (fcc).

- Hexagonal alignment
- Square packing associated with <100> planes
- Square packing associated with <111> planes

Properties of colloidal crystals

The arrangement in a fcc structure produces a periodic variation in refractive index.

\[ \Gamma - L \text{ space} \]

It's possible to tune the position of the Stop band varying the dimension of the NPs.

Direct colloidal crystals

\[ D = 236 \text{ nm} \]

\[ D = 225 \text{ nm} \]
Properties of colloidal crystals

Direct opal structures

\[ \lambda = 2 \times 0.816 D \left( n_{\text{eff}}^2 - \sin^2 \theta \right)^{1/2} \]

\[ \begin{align*}
    d_{111} &= \sqrt{\frac{2}{3}} \cdot D \\
    n_{\text{eff}}^2 &= n_{\text{NPs}}^2 \cdot f + n_{\text{medium}}^2 \cdot (1 - f)
\end{align*} \]
These heterostructures are created by using multilayer deposition systems suitable for wide applications in manufacturing integrated photonic crystal chips, such as broadband reflective mirrors and/or multi-frequency optical Bragg filters.

“Exploiting” depositing on the SiO$_2$ NPs colloidal film opal structures of PS that present different dimension in size.
Optical Properties of HTs

\[ \lambda = 2 \times 0.816 D \cdot n_{\text{eff}} \]

presence of a **double peak** centered at about **800 and 700 nm**.

Formation of **two photonic layers** occurs and a **good ordering** of the structures realized is evident.

- the position of the stop bands of HT match the position of the stop band of single layers.
- this behaviour can be seen as just a **superposition** of the properties of each individual layer.
Direct Opal as template

Direct opal used as a scaffold for formation of Inverse structure

1) Infiltration

2) Removal of beads

3) Inverse colloidal crystal

Photonic Band gap

Bragg’s Law
Properties of inverse structure

Silica inverse structure

Negative replica

Large surface area

Porous material

Possible applications

- **Strain sensor**
- **SERS substrate**
Strain Sensor

Material: *Changing the structural color* under an *external stimulus*

\[ \lambda = 2 \cdot d_{111} \cdot n_{\text{eff}} \]

**Blue shift** of the wavelength of the diffraction peak as a function of the *applied strain*

**How it works?**

**Initial configuration:**
- light source
- light detector
- PDMS elastomer
- PS beads
- polystyrene sphere
- support

**Strained configuration:**
- axial elongation
- transversal contraction

\[ \varepsilon = \frac{\Delta l}{l} \]

Recognize this by *naked eyes*
**Experimental validation**

**Initial**

![Initial image](image1)

**Applied strain**

![Applied strain image](image2)

**Experimental set-up**

![Experimental set-up image](image3)

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Peak position **blue shifts** from 583 to 550 nm

the position of the peak does not change significantly,
Inter planar distance remains constant for the applied strain, since the PS spheres are in contact with each other.

Possible applications

- Strain sensor
- **SERS substrate**

*Metallo – dielectric structures*
Unique optical properties that combine: the localized surface plasmon resonance of Au NPs with the PBG features of colloidal crystal structure.

Chemical Sensor and SERS substrate
Fabrication of metallo-dielectric structures

based on the realization of an inverse silica opal and immobilization of gold nanoparticles on the silica network

Schematic diagram:

(a) using polystyrene and silica solution, an infiltrated opal structure is obtained;
(b) annealing and sintering processes form an inverse silica opal (ISO) structure;
(c) functionalization of the ISO structure with 3-aminopropyltriethoxysilane (APTES);
(d) immobilization of Au Nps on silica network.
Gold nanoparticles

How to prepare?

Turkevich Method (1951)

Reduction of Gold ion by citrate ions

![Diagram showing the formation of gold nanoparticles from chloroauric acid and sodium citrate](image)

chloroauric acid

LSPR = 520 nm
**Structural Properties**

*Inverse ordered structure is still present after immersion process*

**hollow regions of the air spheres**

(well ordered in a triangular lattice corresponding to the (111) planes of a fcc crystalline structure)

**inner dark holes**

(representing the point of contact between each templating sphere and its 12 nearest neighbors)

*After 2 h immersion time*

*Au Nps are attached/immobilized on the network of the ISO system*

*After 10 h immersion time*
Optical Properties of MDCS

**Unique optical properties** that combine:
the **localized surface plasmon resonance** of Au NPs
with the **PBG features** of colloidal crystal structure

**Plasmon peak**

**Diffraction peak**

- (a) inverse silica opal
- (b) MDCS_1h
- (c) MDCS_2h
- (d) MDCS_4h

**Absorbance** vs. **Wavelength (nm)**

- **520 nm**

**Au Nps Colloidal solution**
Raman Signal Enhancement

MDCS systems have been tested as SERS substrate

\[ \text{benzenethiol (BT) as a probe molecule} \quad 1 \times 10^{-3} \text{M} \]

using a 10 s accumulation time, incidence power 100 µW.

to evaluate the efficiency of the MDCS

we have compared the Raman signal obtained for these structures with those collected:

b) on a gold film (GF) deposited by sputtering

c) on ISO spotted with a 5 µl drop of pure BT and left to dry out (ISO_BT).
Raman Signal Enhancement
Conclusions

• Fabrication and Properties of opal structures

• Strain Sensor

• SERS Substrate
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