Characterization techniques for nanostructured materials and their pitfalls

(ECONAM FP7 project)
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Classification of nanostructured materials (NSM) by their linear EM properties. Text

- **Bulk passive structures** (N>4-5 Unit Cells)
- **Optically dense bulk structures** \(d<<\lambda\)
- **Non-resonant materials:**
  - **Non-EM applications, EM applications,**
  - Thick films, optically large samples, Thin films and island films,
  - Radiofrequency Magnetic Media and Nanomagnets, Magneto-Optical Media
- **Plasmonic and polaritonic MTM:**
  - Dipole arrays, Multipole arrays, Resonant Photonic Crystals, Resonant scattering media
- **Optically sparse bulk structures** \(d~>\lambda\)
- **Nanostructured Photonic Crystals, Scattering media (resonant and non-resonant)**
- **Surface passive structures** (N<4-5 Unit Cells)
  - \(d<<\lambda\) Dense gratings  \(d~>\lambda\) Diffraction gratings,
  - **Non-resonant, Resonant**
  - Planar MTM, Vertically Aligned Nanorods
- **Active nanostructures** (of quantum dots and wires, dye-doped nanoporous and liquid crystals matrices, etc). Out of scope
Classification of NanoStructured Materials (NSM) by their linear EM properties. Chart

Passive NSM

I. Nanostr. Bulk mat.

II. Nanostr. Surfaces

II1. Opt. Dense gratings

II11. Constit. non-resonant in optics

I11a. Non-EM applications

II1b. EM applications

I12. Constituents resonant in optics

I12a. Dipole arrays

II1b1. Rad. Mag. Comp.

I11a2. Opt. thin

II11b. EM applications


II111. Constit. resonant in optics

I12c. Multipole arrays

II21. NS Photonic Crystals


II21b Const. Non-Res. In Optics

II22. NS Scattering Media

II22a Const. Non-Res. Scatt. Media

II22b=I12c Res. Scatt. Media

II111a. Planar constituents

Regular arrays of vertically aligned rods, tubes etc.

II111b. Opt.thick

II111c. Opt.thin
Explanation of the chart

Metamaterials

- Scattering (non-transparent) media
  Adopted optical characterization: $Q_E$, $Q_A$

Bulk uniform concentration media

- Adopted optical characterization: $\varepsilon$, radio characterization: $\varepsilon, \mu$. (Bianisotropy is out of scope)

Photonic crystals/EBG

- Adopted optical/ radio characterization: stopbands (bandgaps).
  Additionally: Brillouin dispersion diagram, Fresnel isofrequency surfaces.

Diffraction gratings

- Adopted optical characterization: $D(\lambda,m)$, $\Delta\lambda(m)$, $I_{\text{norm.}}(\lambda,m)$

Mesoscopic layers

- Adopted optical characterization: $Q_E$, $Q_A$, $|R(\lambda)|$, $|T(\lambda)|$
Pitfalls (observations from literature survey)

- Referring a metamaterial to a wrong class. (Diffraction gratings, mesoscopic layers, photonic crystals described as a bulk medium sample)
  
  100s papers. A book

- Ignoring the anisotropy. (Treating a component of material parameter tensor as an isotropic $\varepsilon$ or $\mu$)
  
  10s papers. A book

- Ignoring the bianisotropy. (Describing the bianisotropic material in terms of only $\varepsilon$ and $\mu$)
  
  Some papers

- Ignoring spatial dispersion effects in dipole-type bulk metamaterials
  
  10s papers. 2 books

- Ignoring the problem of the spread boundary of bulk metamaterial samples
  
  100s papers. 3 books
Scattering media (incl. Plasmonic)

Random CNT

Clusters of nanoclusters

Clusters of nanoislands and nanoparticles

SiO2 Raspberries

Au Nanoparticles /Si core

(b) Cu@Ag

(d) Ag
Bulk plasmonic, \( d \ll \lambda \)

1) Dipole materials. 2) Photonic crystals

Bulk powe: Au particles 15 nm

Dipole MTM (modest resonant slow-wave factor)

Scattering Media with Resonant Absorption

Plasmonic Photonic Crystals (High resonant slow wave factor)

Multilayer/random Ag or Au NanoParticles
Scattering sample’s characterization: absorption, extinction, scattering cross sections

\[ F = \int \mathbf{S} \cdot d\Sigma, \quad F = F_s + F_i + F_{is} = F_s + F_{is}, \]
\[ F_s + F_{is} - W_a = 0, \quad F_{is} \propto \text{Im}(\mathbf{E}_{FS} \cdot \mathbf{E}_i^*) \]
\[ QA = \frac{W_a}{E_{i}^2} = \frac{F}{E_{i}^2}, \quad QS = \frac{W_s}{E_{i}^2} \]
\[ QE = \propto \frac{\text{Im}(\mathbf{E}_{FS} \cdot \mathbf{E}_i)}{E_{i}^2} = \frac{W_a + W_s}{E_{i}^2} \]

QA, QS, QE – mesoscopic parameters
Photonic crystals experimental characterization

1. **Band-gaps detection** [56].
2. For low-loss structures: phase(T) – dispersion along ΓX [57]

**Band-gaps detection** [58]
Photonic crystals treated as media

Three-dimensional optical metamaterial with a negative refractive index

Jason Valentine, Shuang Zhang, Thomas Zentgraf, Erick Ulm-Avila, Dinesh A. Geno, Kor Brettschneider, and Xiang Zhang

PHYSICAL REVIEW B 78, 155102 (2008)

Light propagation in a fishnet metamaterial

Analytical theory of wave propagation through stacked fishnet metamaterials

G. Marzella, T.J. Jenning, F. Mero, and P. Mille

6 July 2009 / Vol. 17, No. 14 / OPTICS EXPRESS 11582

Cladding ($\varepsilon=10+i1$)

Acceptable

Photonic approach to making a material with a negative index of refraction

Gennady Shvets

$$\varepsilon_{\text{eff}} = \left( \frac{1}{\varepsilon_{\rho}} + \frac{1 - \cos \chi_{\nu} b}{\chi_{\nu} \sin \chi_{\nu} b} \right) \left( \frac{1}{\varepsilon_{\rho} \chi_{\nu}} + \frac{1 - \cos \chi_{\nu} b}{\chi_{\nu} \sin \chi_{\nu} b} \right)^{-1},$$

$$\mu_{\text{eff}} = 1 - \frac{c^2 \chi_{\nu}}{\omega^2 \sin \chi_{\nu} b} \left( \frac{1}{\varepsilon_{\rho} \chi_{\nu}} + \frac{1 - \cos \chi_{\nu} b}{\chi_{\nu} \sin \chi_{\nu} b} \right)^{-1},$$

unit cell of $p = 860$ nm, $\lambda$ of 1,475 nm, the index of refraction is approaching zero

Acceptable

ABC are required
Photonic crystal mimics the homogeneous medium only under

- **2 conditions:**
- **Geom. isotropic lattice**
- **Special environment**

   Electric field when the structure is surrounded by a homogeneous material with $\varepsilon = 5.7$ and $\mu = 0.175$ (both positive), i.e., a material having the same impedance as in our interpretation is that in our case the photonic crystal mimics a homogeneous material with $\mu_{\text{eff}} = 1/\varepsilon_{\text{eff}} \neq -1$.

### Special medium surround: a weakly subwavelength image arises

 Vacuum surround. Negative refraction but no subwavelength effects

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*PRL 97, 073905 (2006)*

Photonic Crystal Lens: From Negative Refraction and Negative Index to Negative Permittivity and Permeability

T. Decoopman, G. Tayeb, S. Enoch, D. Maystre, and B. Gralak
Diffraction gratings

Handbook of microscopy for nanotechnology (N. Yao, Z.L. Wang 2005 Kluwer)

(Grigorenko 2005)

(Shalaev, 2003)
Characterization of diffraction gratings

- Normal incidence $\lambda>d$, oblique incidence $\lambda>2d$:
- $|R|$ or $|T|$ $(\lambda)$. Plasmonic gratings: absorption at Wood anomalies $W_a=1-|R|^2-|T|^2$.
- Normal incidence $\lambda<d$, Oblique incidence $\lambda<2d$:
- Angular dispersion $D(\lambda, m)$, where $m=\pm1.. \pm[d/\lambda]$ grating spectral orders.
- 3. Free intervals of dispersion $\Delta\lambda(m)$. 4. Normalized intensity distribution $I_{\text{max}}(\lambda,m)$.

![Diagram of diffraction gratings](image)

Incident beam → Transmitting grating → Scanning detectors (matrix detectors, spectrometers) → Reflecting Grating
Diffraction gratings treated as bulk media

Cut-wire pairs and plate pairs as magnetic atoms for optical metamaterials

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Nanofabricated media with negative permeability at visible frequencies

A. N. Grigorenko, A. K. Geim, H. F. Gleeson, Y. Zhang, A. A. Firsov

Vol 438/17 November 2005 doi:10.1038/nature04242
Vertically aligned nanorods

Plasmonic (gold) nanorods
- Modest slow-wave factor
- Can be treated as uniaxial dielectric if period $<\lambda$

CNT
- Huge slow-wave factor (>100)
- Wire medium
- ABC are obviously required

Other vertically aligned Nanorods (InP, TiO2 etc)
Variable-Angle-Spectrometric Ellipsometry

\[ \tan(\Psi) \cdot e^{i\Delta} = \rho = \frac{r_p}{r_s} \]
\[ |r_p(\lambda)|, |r_s(\lambda)| \]

1. linearly polarized light...
2. reflect off sample...
3. elliptically polarized light!

Basic configuration for reflection ellipsometry.

Known fitting procedure implies:
1. Bulk medium (at least 5-6 molecules across)
2. Not metamaterials ($\mu=1$)
Characterization techniques for plasmonic and CNT nanostructured surfaces

Reported experiments:
MTM with planar plasmonic elements, N=1-2:
  a) Used method: NRW. Results: Not adequate.
  b) Used method: spectroscopy. Results: Incomplete.

Reported theory:
1. Holloway et al.: surface electric and magnetic tensor susceptibility.
   Simovski: electric and magnetic grid impedance.
   Not sufficiently developed and never checked
2. Plasmonic nanowires and CNT.
   Wire medium models with tensor \(\varepsilon(q)\). Insufficiently developed:
   (no additional boundary conditions)
Nicholson-Ross-Weir (NRW) technique in optics

Complex $R, T \rightarrow n, z = \sqrt{\mu/\epsilon}$

Detector (Spectrometer) + Interferometer
beamwidth ~ $(2-5)\lambda$

Layer sample

Nanostructured material

1952, Schopper

Complex $R \rightarrow$ Complex $n$

Mirror

Weakly dispersive $n$ (see O. Heavens, Optics of Thin Films)
NRW method (theory for uniform slabs)

Replace the finite-thickness lattice by an “equivalent” continuous layer

\[ T = \left[ \cos(nk_z d) - \frac{i}{2} \left( Z + \frac{1}{Z} \right) \sin(nk_z d) \right]^{-1} e^{-ik_z d}, \]

\[ R = -\frac{i}{2} \left( Z - \frac{1}{Z} \right) \sin(nk_z d) T e^{ik_z d}, \]

Then:

\[ n = \pm \cos^{-1} \left( \frac{1 - r^2 - t^2}{2t} \right), \]

\[ Z = \pm \left[ \frac{(1 + r)^2 - t^2}{(1 - r)^2 - t^2} \right]^{1/2}, \]

where \( r = R \) and \( t = T e^{ik_z d} \)

\[ \epsilon_{\text{eff}} = n/Z, \]

\[ \mu_{\text{eff}} = nz. \]
However, remember that

NRW was developed NOT for metamaterials!
Equivalence for a given case≠adequacy

Being applied for
1) Non-bulk (surface) structures
2) Nanostructured photonic crystals
   and even
3) Bulk nanostructured media with resonant constituents

these method lead to ”beating the physical limits”= violation of physical laws.
Results of wrong applying the NRW method

- Violation of locality (passivity, causality, II law of thermodynamics)
- Extracted $\varepsilon$ and $\mu$ are not applicable for oblique incidence, for narrow wave beams, for evanescent waves
- Polaritons are neglected

Forbidden

Antiresonance

 Similar results:

100s papers and 3 books
Experimental characterization for bulk plasmonic dipole MTM and plasmonic photonic crystals

Reported experiments:
1. Dipole plasmonic MTM. Used method: NRW. Results: indequate
2. Plasmonic photonic crystals. Used method: NRW. Results: indequate

Reported self-consistent theories:
1 Dipole plasmonic MTM:
1.1 Bulk (Simovski): Not sufficiently developed, not checked
1.2 Planar (Holloway et al.): The same
2. Plasmonic photonic crystals:
2.1. Gralak et al. Weakly developed, 2.2 Shvets-Urzhumov: Insufficiently developed, not checked
2.3 Silveirinha: The same

Reported controversial theory:
Arbitrary resonant lattices (Felbaq et al.). Difficult to accept. Not checked
Correct characterization of dipole-type bulk metamaterials (no experimental results yet)

Material Parameters of Metamaterials (a Review)

C. R. Simovski

Transition layers:
- refraction index + wave impedance

Same parameters as for the infinite lattice

Resonant particles
Antiresonance explanation

\[ n^2 = \varepsilon_B \mu_B = \varepsilon_{\text{stat}} \mu_L, \]

\[ \varepsilon_B = \varepsilon_{\text{stat}} \frac{1 + A \omega^2}{(\omega_0^2 - \omega^2 - i\Gamma \omega)} \]

\[ 1 > B > A \quad \varepsilon_B \text{ is "antiresonant"} \]

"EMP" extracted by NRW

Magnetic Mie resonance

Local EMP
“Artificial magnetic” when and only when: $\omega = \omega_{\text{mag}}$ and $q = qy_0$.

If $q = qx_0$, this is an artificial dielectric.

In all other cases – more material parameters are needed.

Never "artificial magnetic"

$k(1) - M + Q$
$k(2) - another Q$
$k(3) - third Q$
"Magnetism" due to phase shift between two elements (A and B) of an open inclusion – 100s papers

- Quadrupoles and octupoles can be neglected only for

In other cases (dual bars, U-shaped SRRs etc)

\[
D_i = \varepsilon'_{ij} E_j + j \xi'_{ij} H_j + b_{ijkl} \nabla_k \nabla_l E_j,
\]

\[
B_i = \mu'_{ij} H_j - j \xi'_{ij} E_j,
\]

Or

\[
D_i = \varepsilon_{ij}(\omega, q) E_j, \quad \varepsilon_{ij}(\omega, q) = \varepsilon^{(0)}_{ij}(\omega) + j \gamma_{ijk} (\omega) q_k + j \gamma_{ijkm}(\omega) q_k q_m + \ldots
\]

\[
H = \mu_0^{-1} B.
\]

In both cases ABC are required!
Metasurfaces (no experimental results, yet)

Electric and magnetic surface susceptibilities

A discussion on the interpretation and characterization of metafilms/metasurfaces: The two-dimensional equivalent of metamaterials

Christopher L. Holloway a,⁎, Andrew Dienstfrey b, Edward F. Kuester c, John F. O’Hara d, Abul K. Azad d, Antoinette J. Taylor d

MTM mesoscopic layer (no cross-polarization and spatial dispersion)

\[ \mathbf{J}_e = \chi_e \mathbf{E}_\text{tan}, \quad \mathbf{J}_m = \chi_m \mathbf{H}_\text{tan}, \]

\[ \chi_{e,m}^{TE,TM} = \begin{pmatrix} \chi_{xx} \\ \chi_{yy} \end{pmatrix} \]

1-2 inclusions

Effective surface

Substrate

Substrate
Conclusions

- There are many pitfalls in the NSM characterization
- Classification of NSM is very important to select the proper characterization parameters to retrieve
- To explain the physical meaning of retrieved parameters is very important
- There are self-consistent theories of NSM characterization, however not sufficiently developed and never experimentally checked!
- For some NSM even no any theory yet!
- Inadequate characterization method (wrong interpretation) –
- impasses in the theory and insufficient practical achievements –
- metamaterials are compromised as such – no more support