



# UNIVERSITÀ DI PISA

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## SPECTROSCOPY AND MICROSCOPY OF NANOMATERIALS / SPETTROSCOPIA E MICROSCOPIA DEI NANOMATERIALI

**FRANCESCO FUSO**

Anno accademico **2021/22**  
CdS **FISICA**  
Codice **383BB**  
CFU **6**

Moduli	Settore/i	Tipo	Ore	Docente/i
SPETTROSCOPIA E MICROSCOPIA DEI NANOMATERIALI	FIS/03	LEZIONI	36	FRANCESCO FUSO

Obiettivi di apprendimento

### *Conoscenze*

- Fondamenti di elettromagnetismo, ottica e interazione radiazione/materia;
- Fondamenti di microscopia elettronica (SEM e TEM);
- Microscopia ottica di fluorescenza, confocale e oltre il limite di diffrazione (STED, PALM, STORM, 4Pi, light-sheet, etc.);
- Microscopia Raman e Raman coerente (SRS, CRS, CARS, resonant Raman, etc.);
- Fluorescenza da cromofori e proprietà ottiche e confinamento quantico in nanostrutture di semiconduttori (QD, core-shell QD);
- Plasmonica superficiale e localizzata (SPP, LSPR), microscopia di leakage, enhancement di fluorescenza e substrati SERS;
- Fondamenti di nano-fotonica, sistemi a band-gap fotonico, metamateriali;
- Microscopie e spettroscopie a scansione di sonda (STM, AFM, SFM, EFM, etc.) e a campo ottico prossimo (SNOM, r-SNOM, TERS).

### *Modalità di verifica delle conoscenze*

Le conoscenze acquisite dagli studenti e dalle studentesse saranno puntualmente verificati durante l'anno tramite discussioni e approfondimenti in classe. L'esame finale è orale e può includere la preparazione di brevi seminari di approfondimento basati su recenti progressi nel settore.

### *Capacità*

Alla conclusione del corso gli studenti e le studentesse avranno acquisito la capacità di analizzare problemi di ottica che coinvolgono nanomateriali, sia per l'analisi delle proprietà su scala locale che per lo sfruttamento delle specifiche caratteristiche ottiche in dispositivi e metodi. Inoltre avranno ricevuto nozioni di base di nanofotonica, metamateriali, metodi anche non ottici a scansione di sonda. Pur avendo un carattere prevalentemente fisico di base, il corso favorisce lo sviluppo di capacità inter-disciplinari, strettamente connesse con altri settori, in particolare biofisica e biomateriali.

### *Modalità di verifica delle capacità*

Durante il corso gli studenti sono incoraggiati a discutere gli aspetti di maggior interesse nel corso delle lezioni. Inoltre le capacità acquisite possono essere verificate anche attraverso la preparazione di brevi presentazioni su argomenti inerenti il corso.

### *Comportamenti*

Gli studenti e le studentesse acquisiranno sensibilità specifica nel trattare argomenti di nanomateriali da un punto di vista interdisciplinare, che, partendo dalle proprietà fisiche di base, arriva alle applicazioni attuali e di maggior risonanza.

### *Modalità di verifica dei comportamenti*

L'atteggiamento di apertura interdisciplinare degli studenti sarà verificato durante le discussioni in classe, anche attraverso specifici test basati su brevi presentazioni.

### *Prerequisiti (conoscenze iniziali)*

Conoscenze base di elettromagnetismo e fisica dei materiali, incluse basi di meccanica quantistica.



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## Indicazioni metodologiche

- lezioni frontali
- discussioni in classe
- visita di laboratori e discussione di pratiche sperimentali

## Programma (contenuti dell'insegnamento)

### 1. Generalities on the topic

Aims and motivations for spectroscopy of nanomaterials, specific properties of nanostructures including biomimetics, size limits of the nanoworld, technological issues. The main problem of optics in the nanoworld: interference and diffraction in optics. Electron microscopy as a benchmark and a reference for nanoscopy: general instrumental configurations of SEM and TEM, main contrast mechanisms, secondary and backscattered electrons. Spectroscopies with electrons/X-rays: AES, EDS/EDAX, XPS.

### 2. Optical microscopy/spectroscopy and nanomaterials

Ray optics, lenses and magnification in a microscope, Gaussian beams and focusing, diffraction and interference. Few words on Fourier optics: PSF and resolving power according to Rayleigh, Abbe, and Sparrow criteria. Conventional optical microscopy and some variants: polarization, differential interference, white light profilometry. Fluorescence microscopy, organic chromophores, reminders of molecular levels and transitions, biophysical applications: epi-fluorescence, illuminations issues, dark field microscopy. Confocal configurations of optical microscopy/spectroscopy, examples. MicroRaman, coherent Raman (CRS/CARS) and other advanced spectroscopies at the micro-scale, examples and measurement of various material properties at the micro- and nanoscale.

### 3. Super-resolution optical microscopies

Stimulated emission in a multi-level system, pumping and saturation. Spiral phase plates, optical vortices, doughnut modes. STED, resolving power, examples of applications. Other super-resolved microscopies (PALM, STORM, 4Pi, light-sheet, double beam, etc.)

### 4. Quantum confinement and optical properties of semiconductor nanostructures

Reminders of bulk semiconductor properties, direct and indirect transitions. Reminders of quantum mechanics and the problem of the potential well (infinite and finite). Confinement and 2-D (quantum wells), 1-D (quantum wires), 0-D (quantum dots) nanostructures: quasi-discrete levels, interband and intraband transitions, sub- and mini-bands, excitons in confined systems, density of states and dimensionality. Absorption and emission properties in quantum dots, including core-shell systems, related technologies and some applications, in particular in optical nanoscopy and nano-photonics.

### 5. Plasmonics at a surface

Introduction to plasmonics: plasma frequency in metals and bulk plasmons, interband transitions and their role, complex dielectric constant and refractive index, Drude model. Surface plasmon polaritons at plane interfaces: solution of the electromagnetic problem leading to longitudinal e.m. waves stemming from surface charge oscillations, evanescent behavior and dispersion relation. Excitation of plasmon modes: through evanescent waves, including near-fields, gratings, high aperture objectives (TIRF microscopy). Visualization of plasmon modes via leakage microscopy (Fourier plane imaging) and collection-mode near-field microscopy. Surface plasmon spectroscopy and applications. Main optical properties of graphene and plasmonics in graphene: examples with apertureless near-field microscopy.

### 6. Plasmonics at a nanoparticle

Emission of radiation in the far-field from oscillating dipoles according to the Maxwell equations, Larmor's formula. Scattering from nanostructures: dipole and multipole contributions (Rayleigh and Mie); Clausius-Mossotti expression of dielectric constant. Localized surface plasmon resonances, optical extinction, dispersion relation, a few words on geometrical issues (beads, wires and other shapes): role of localized plasmon resonances in optics and photonics, plasmonic nanostructures as markers in microscopy, sensing applications, a few words on plasmon-based therapeutics, local field enhancement and the concept of nano-antennas, transfer of e.m. energy through plasmonic waveguides. SERS-active substrates for enhanced Raman spectroscopies: examples.

### 7. Photonic band-gap structures and metamaterials

Bragg interference in planar and non-planar structures, transmission and reflection, occurrence of a photonic band-gap: similarities with the electron wavefunctions in solid-state materials and with the energy gap in crystalline semiconductors. Survey of photonic band-gap nanostructures in one and two dimensions, including fabrication. Examples of applications: photonic crystal fibers and super-continuum generation, waveguides and photonic components, optical spectroscopies, laser cavities. Basics of metamaterials: tuning the e.m. properties of a system through structural engineering, control of the magnetic permeability, single and double negative materials, negative refractive index; open possibilities and perspective applications of metamaterials in different fields.

### 8. Scanning probe microscopies for the spectroscopy of nanomaterials: STM

Concepts and basic elements of SPMs: piezoelectric scanners and probes, the invention of STM and the role of feedback. Reminders of tunnel effect including semi-classical approximations for trapezoidal barriers, role of material properties (work function) and related spectroscopies, examples. Advanced quantum pictures of tunneling: role of local density of states and bias-based spectroscopies, s- and p-wave tunneling and functionalized probes, observation of "molecular orbitals" in isolated molecules, examples including UHV and low-temperature STM.

### 9. AFM and some variants

Measurement of small forces through a cantilever and optical lever, technology of AFM probes. Forces between a tip and a surface: general



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considerations, Hertzian contact, Hamaker attraction. Operating modes of an AFM: contact vs tapping mode, modulation/demodulation (amplitude, phase, frequency), phase maps and their physical interpretation (in intermittent contact), constant amplitude and multi-modal AFM. Examples, including in liquid operation, and related force spectroscopies. Lateral forces and nanotribology, electric and piezoelectric force microscopy with examples, nanoindentation and spectroscopies for the investigation of mechanical properties at the nanoscale.

### 10. Optical near-fields and SNOM

General concepts of near-field, calculation of the near-field produced by an oscillating dipole, ideal problems (Bethe-Bouwkamp), evanescent character and practical implementations. Basics of near-field microscopy in the emission mode: probes and related technologies, the shear-force method, range of spectroscopies accessible by SNOM, including collection mode of operation. Examples of fluorescence and label-free spectroscopy with biological materials, applications to surface and localized plasmons. Polarization-modulated spectroscopies and applications in the near-field. Apertureless (scattering) SNOM: pros and cons, single molecule fluorescence, IR spectroscopy in the near-field, a few words on THz SNOM. Tip-enhanced Raman spectroscopy and examples of TERS.

### Bibliografia e materiale didattico

La bibliografia specifica per ogni argomento trattato, inclusa anche un'ampia raccolta articoli di ricerca disponibile nel sito di e-learning, è comunicata agli studenti e studentesse al termine delle lezioni.

### Indicazioni per non frequentanti

Mettersi in contatto preliminarmente con il docente e seguire il materiale didattico fornito via web sulla pagina di e-learning.

### Modalità d'esame

Esame finale orale, parte del quale può essere sostenuta basandosi su una breve presentazione su argomento concordato.

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