Optical Properties of Metal Nanoparticles and Nanoparticle Assemblies

Review:

Wei, Q.; Wei, A. In Supramolecular Chemistry of Organic–Inorganic Hybrid Materials (Chapter 10), Mañez, R. M.; Rurack, K., Eds.; Wiley and Sons: New York, 2010; pp. 319-349
Size effects on localized SPRs

Surface scattering of oscillating electrons: plasmon lineshape ($\Gamma$) broadens with $1/R$

Phase retardation: redshift and broadening of $\lambda_{SP}$ for particles greater than $L_E$, the electron mean free path (40-50 nm)

Higher-order plasmon resonances: increase in probability with larger particle size (also a function of $L_E$)

Dielectric effects: influence on LSPR wavelength

LSPRs and FWHM linewidths of Ag nanoparticles in different environments (calculated)


Solvatochromatism in polymer-stabilized 16-nm Au nanoparticles

Metal nanoparticles as optical labels

A. Size-dependent optical extinction

Ag-enhanced detection of Au nanoparticle (NP) label:

Detection limit: ~50 fM

B. Resonant light scattering

Size-dependent color response (Au NPs):

- <50 nm: $\lambda_{LSPR} = 520-530$ nm (green)
- 80 nm: $\lambda_{LSPR} = 560-570$ nm (yellow)
- 100+ nm: $\lambda_{LSPR} = 580+$ nm (orange)


Detection of DNA hybridization by darkfield (scattering) microscopy:
Aggregation-induced amplification of light scattering

DNA-induced aggregation of 30-nm Au NPs monitored by dynamic light scattering (DLS)

- low picomolar (pM) resolution;
- sensitive to base-pair mismatches


Metal nanoparticles as optical labels

C. Aggregation-induced shifts in plasmon resonance (colorimetric assay)

Ex. 1. DNA-induced aggregation of Au nanoparticles

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Individual particles: uncoupled LSPRs

Aggregated particles: collective SPR


Variations in “melting” (dissociation) temperatures, $T_m$, as a function of base pairing:

(A) complementary target
(B) no target
(C) complementary to one probe
(D) a 6-bp deletion
(E) a 1-bp mismatch
(F) a 2-bp mismatch
Aggregation-induced shifts in plasmon resonance (cont’d)

**Ex. 2:** Lectin-induced aggregation of 9-nm Au NPs, with thiolated lactose (glyco-NPs)

After lectin addition (µg/mL): (a) 0; (b) 5; (c) 10; (d) 20; (e) 50. (solid line) redispersed NPs, after adding excess galactose.


For other examples of Au nanoparticles in colorimetric assays, see: *Inorganic Nanoprobes for Biological Sensing and Imaging*, Eds. H. Mattoussi, J. Cheon, Artech House:New York, 2009; Chapter 8 (Rotello and coworkers)
Metal nanoparticles as bio/chemical sensors

Adsorption-induced shifts in surface plasmon resonance (SPR)

Surface adsorption changes the local refractive index of thin (50-nm) Au film, causes shift in “critical angle” for SPR absorption

Works best for detecting biomolecular adsorption (e.g., proteins); small-molecule detection is harder

Nanoparticle-enhanced SPR detection of DNA oligonucleotides:

He et al, J. Am. Chem. Soc. 2000, 122, 9071

Nanoparticle-enhanced SPR detection of DNA oligonucleotides:

He et al, J. Am. Chem. Soc. 2000, 122, 9071

Reliable detection limit: ~10 pM for 24-mer
Anisotropic metal NPs as bio/chemical sensors

Adsorbate-induced shifts in LSPR: greater sensitivity


![Image of nanoprisms and related chemistry](image)

- **A** Bare Ag nanoprisms
- **B** Nanoprisms after modification with 1 mM 1:3 11-MUA/1-OT
- **C** Nanoprisms after modification with 1 mM biotin
- **D** Nanoprisms after exposure to 100 nM SA ($\Delta \lambda = 27$ nm)

![Graph showing extinction vs. wavelength](image)

- **A** Biotinylated nanoprisms
- **B** Exposure to 100 nM SA ($\Delta \lambda = 27$ nm)
- **C** Amplification of SA response using biotinylated Au colloids ($\Delta \lambda = 56$ nm)

**Dynamic range of $\Delta$SP**

- $\Delta R_{max} = 26.5$ nm
- $K_{a, surf} = 10^{11}$ M$^{-1}$
- LOD $< 1$ pM

![Graph showing dynamic range](image)
Anisotropic metal NPs as bio/chemical sensors

Changes in surface dielectric = LSPR shift

Single-nanoparticle SPR spectroscopy

(A) Ag NP before and after adsorption of C16-thiol.
(B) LSPR response vs. thiol chain length.

Anisotropic nanoparticles are more sensitive to local changes in surface dielectric; measured in refractive index units (RIU)

Anisotropic metal nanoparticles: Au nanorods

Au NRs: Tunable resonances in the NIR

Longitudinal SP ($\lambda_{\text{max}}$)

Transverse SP

"Biological window" in tissue at NIR wavelengths:

Attenuation is minimized between 750 nm and 1.3 $\mu$m

SP modes as a function of aspect ratio:
Link and El-Sayed, J. Phys. Chem. B 1999, 103, 3073
Seeded growth using micellar surfactants (CTAB):

AgNO₃, CTAB
AuCl₄, ascorbic acid
15-60 min

3-nm Au particle seeds


Two-stage growth kinetics: effect on LPR wavelength

![Graph showing two growth stages and LPR wavelengths](image)

1st growth stage (fast): dumbbell-shaped NRs (stabilized after Na₂S)
2nd growth stage (slow): Cylindrical NRs

![Images of NRs grown in two stages](image)
Other anisotropic Au nanoparticles

Nanoprisms (by nanosphere lithography)


Nanosheells *(SiO$_2$@Au)*

Pentagonal bipyramids *(decahedra)*

Nanocages (growth on Ag nanocubes, with galvanic displacement)

Nanostars (seeded growth from Au NPs)
More examples of LSPR biosensing

Antibody-labeled Au nanorods for multiplex biosensing


Real-time LSPR with antibody-labeled pentagonal bipyramids

λ_{LSPR} = 750-900 nm
LSPR sensitivity: 280-380 nm/RIU

Collective optical properties of NP assemblies

Models of electromagnetic coupling between particles: large shift in collective SPR

Discrete dipole approximation (DDA) of 30-nm Ag particle dimer as a function of separation (S)


Simulation of (GMT) collective SPR of Ag NPs assembled into different geometries


Challenges in comparing experiment and theory:

- calculations for particle sizes greater than 40 nm (quasistatic limit)
- Strong, highly nonlinear plasmon coupling between closely spaced particles (< 50% of diameter)
- Accounting for structural or surface charge defects; establishing local dielectric constants ($\varepsilon_d$)