Plexcitonic optical response of core-shell hybrid nanoparticles

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Part of the work was conducted at the Physics Dept., METU

“Hybrid devices consisting of nanoscale optical, electronic as well as molecular-scale materials hold great promise for enhancing and achieving new functionalities based on light-matter interactions [1].”


There is considerable current interest in coupling excitonic and plasmonic states as a means of modifying the OR of the noble metal nanostructures, and thereby to develop new photonic devices that combine their nanoscale optical responses. Such systems hold potential for tunable nanophotonic devices for imaging, chemical sensing, and resonance energy transfer (sensors, switches, lasers, light-harvesters etc.).
Noble metal nanoparticles and localized surface plasmon resonance (LSPR)

Nanostructures of noble metals exhibit collective oscillations of their conduction electrons with respect to the positive ion background in the applied electric field.


Halas *et al.*, *A plethora of plasmonics from the laboratory for nanophotonics at Rice University*. Advanced Materials, 24, 2012.
J-aggregates (JA) and their excitonic states

Interactions among the transition dipole moments (TDM) of the constituent molecules \( \rightarrow \) delocalized excited states/excitonic states \( \rightarrow \) optical response

A sharp, red-shifted absorption band (J-band)
A superstate with a large TDM/oscillator strength
Absorption peaking around typical Au/Ag LSPR
Spectral tuning: different monomeric molecules, different aggregation/coherence lengths

Restriction of the absorbing medium in a nanoscale volume offers the ability to tune the resonance against the dielectric constant (s) of the surrounding (s). “confinement”

Nanoshells: gifts in a gold wrapper

Size is not an effective control for particles <<the excitation wavelength

The systems of nanoshells surpass this scale invariance.

Variable “shell thickness” + Layers of different core, spacer and shell materials

Increased control over the positions, the splitting and the strength of the two LSPRs
Plexcitonic nanoparticles

A plasmonic noble metal nanoshell or a core covered by an excitonic JA shell

Plexcitonic NPs exhibit strong exciton-plasmon coupling. (considerable experimental evidence in the last 5-10 years)

Mixed exciton-plasmon states

Plasmonic states can absorb very well. Excitonic states can fluoresce well.

Tunable nanophotonic devices for imaging, chemical sensing, light-harvesting and lasing.

Extinction spectra of bare gold NPs with different sizes (from 10 to 45 nm). The J-aggregate band (around 586 nm).

Extinction spectra of Au NPs with different sizes coated with J-aggregates.

TEM images

........ As the size of gold particle is tunable, the precise optimization of the strong coupling between the electronic transitions of organic components TDBC and the plasmon modes of the gold NPs is achieved corresponding to a Rabi energy of 220 meV, a value not yet obtained in such a system.......
The OR/plasmonic response of noble metal NPs was grasped well through analytical as well numerical methods (extensively studied in the last two decades). This knowledge was integrated into the interpretation of the OR of the plexcitonic NPs.

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The nanoscale OR of the excitonic shell was ignored at large. (i.e., the nanoshell OR was assumed to be the same as the bulk OR) Such an understanding was absent in the literature.
A hybridization model for the plasmon response of complex nanostructures
Prodan et al., Science, 2003

Plasmon hybridization in metal nanoshells: the interaction between the sphere and cavity plasmons.

The two nanoshell plasmons are antisymmetrically coupled (antibonding) $\omega_+$ plasmon mode and a symmetrically coupled (bonding) $\omega_-$ plasmon mode.

Drude nanoshells have two orthogonal resonances.

Dispersion should not matter.
Orthogonal resonance doublet should also pertain for the organic molecular/ the J-aggregate nanoshells with an adequate dispersion relationship.

The excitonic J-band is a huge TDM that simply oscillates in the applied electric field. Lorentzian dispersion is a reasonable model to start with.
Rationale

It is widely acknowledged that classical electrodynamics provides a reasonable quantitative description of the optical response of noble metal NPs.

If the size of the system is much smaller than the wavelength of the incident light it is sufficient to consider only the dipolar response to light and the quasi-static approximation is appropriate. (Maxwell $\rightarrow$ Laplace)

\[ \alpha(\omega) - \text{polarizability: induced dipole moment/electric field strength} \]

Absorption cross-section: \[ \sigma(\omega) = \text{constant.} \quad \omega \text{Im}[\alpha(\omega)] \]

dielectric function/constants of the core, shell, and medium + structural parameters; core radius, shell thickness

Polarizability acquires its $\omega$-dependence through $\omega$-dependence of the dielectric functions of the core/Drude and the shell/Lorentzian.

Results


*NPs with Lorentzian dispersion/excitonic NPs are blue shifters of the optical resonance(s) contrary to Drude/plasmonic NPs (well-known red shifters).*


*A new methodology is developed in which the functionalities of the dispersive properties of the spherical shell and the nanoenvironment in tuning the OR are clearly separated.*

*This separation allows a convenient control for a bottom-up manipulation of the OR of the spherically symmetric nanoshells with different dispersions.*

*Convenient resonance rulers for the typical Drude (plasmonic) and Lorentzian (excitonic) nanoshells are provided.*

*Optical signature of the Lorentzian nanoshells is an orthogonal pair of resonances. Both are blue-shifted w.r.t. the “bulk resonance.”*

The classical electrodynamics based response of the core-shell hybrid can be understood as a 3-level system of two distinct subsystems: a simple 2-state system in which the plasmon and the blue-most excitonic states are coupled, an uncoupled excitonic state.

This 3-level scheme can explain the key features of the experimental absorption data. The results can be instrumental for the bottom-up engineering of the plexcitonic OR.
Plasmonic response of the intact core

Drude dispersion

\[ \varepsilon_{\text{Drude}}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma_P)} \]

LSPR peak ≈ 680 nm

Au core parameters

- spherical radius = 20 nm
- aspect ratio = 3
- \( \varepsilon_{\infty} = 9.84 \)
- bulk plasmon frequency: \( h\omega_p = 9 \text{ eV} \) (138 nm)
- plasmon relaxation rate: \( h\gamma_p = 70 \text{ meV} \)

embedding medium: water
Excitonic response of the intact shell system

(not identical to the in solution ("bulk") optical response as assumed in the literature at large)

\[ \varepsilon_{\text{Lorentz}}(\omega) = \varepsilon_{\infty} - \frac{f\omega_0^2}{(\omega^2 - \omega_0^2) + i\gamma_0\omega} \]

Lorentzian dispersion

Optical signature of the Lorentzian nanoshells is a blue-shifted excitonic doublet.
Optical response of the plexcitonic system
(Drude core-Lorentzian shell)

Fixed aspect ratio: 3
Fixed shell thickness: (thickness/core radius=0.12)
Different oscillator strengths: 0.03, 0.05, 0.07, 0.09

The splitting (exciton-plasmon coupling?) observed in the experiments is produced faithfully.
Exciton-plasmon coupling leads to a pair of hybridized bands around “the originally degenerate” exciton and plasmon resonances.

The coupling is between the LSPR of the core and the blue-most excitonic transition of the shell. The excitonic state of lower energy is uncoupled.

(Nanoshells offer a pair of orthogonal resonances.)
The plexcitonic spectra can be quantified in terms of a QM 2-state model.
Strong coupling of localized plasmons and molecular excitons in nanostructured silver films

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We report on the resonant coupling between localized surface plasmon resonances (LSPRs) in nanostruc-

A 3-level system of two distinct subsystems: a 2-state system in which the plasmon and the blue-most excitonic states are coupled, an uncoupled excitonic state.

Optical signature of the Lorentzian/excitonic nanoshells is a pair of orthogonal resonances. Both resonances are blue-shifted w.r.t. the “bulk resonance”.
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A 3-level system of two distinct subsystems: a 2-state system in which the plasmon and the blue-most excitonic states are coupled and an uncoupled excitonic state.
Core-shell gold J-aggregate nanoparticles for highly efficient strong coupling applications. 

Extinction spectra of bare gold NPs with different sizes (from 10 to 45 nm). The J-aggregate band (around 586 nm).

For designing the plexcitonic nanoparticles with maximum splitting one should prefer a J-band on the red of the plasmon resonance/ tune the plasmonic resonance on the blue of the in-solution excitonic band.
Overall

In addition to contributing to an increased control over tuning the OR of core-shell plexcitonic NPs for their potential applications, these results can stimulate interest for analytical approaches aiming at a more fundamentally sound understanding of the exciton-plasmon coupling.
A more fundamental understanding of the mechanism of coupling?


Semiconductor-metal nanoparticle molecules: Hybrid excitons and the nonlinear Fano effect
How coherent is the exciton-plasmon coupling?

Possible connection to the real-world: Dynamics of the Rabi oscillations. This will possibly follow experimentally-ultrafast spectroscopy.

Explore the dynamics of excitations in a typical two-state problem, e.g., Stochastic Liouville Equation-add some statistical mechanics.