Coupled plasmonic resonances on biofunctionalized silver nanoparticle-aggregates

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ABSTRACT

The absorption spectra of bio-functionalized silver nanoparticles contained in aqueous dispersions were computed by finite element method and compared to spectra determined by UV-visible spectroscopy. The experimental study has shown that the presence of aggregates resulted in double-peaked spectrum, when the surface of the silver nano-particles was bio-functionalized. The degree of splitting was pH dependent indicating that silver nanoparticles based localized surface plasmon resonance sensors can be used to determine the dependence of aggregation on pH and on biomolecule concentration. Different aggregate-geometries that result in resonance at the measured absorptance maxima were determined by varying the number of silver nanoparticles, and the inter-particle distance in linear and 2D wavy chains, and considering the biomolecule layer surrounding the nanoparticles as a dielectric shell. Versatile relative orientations of the aggregates with respect to the E-field oscillation direction were taken into account by varying the incidence angle of p-polarized light. The near-field distribution along the arrays proved that the primary maxima in the UV involve the spectral effect of quadrupolar modes, while the red-shifted secondary maxima originate from dipolar modes appearing due to coupled plasmon resonances on aggregates elongated along the E-field oscillation direction, and from cross-couplings on versatile non-linear aggregates.

1. INTRODUCTION

- Sensing and detecting devices based on SPR phenomena [1]
- Metal nanoparticles in bio-sensing [2]
- LSPR based bio-sensors: sensitivity, specificity, integration [3]
- Gold nanoparticles (Au NPs): stability, LSPR in visible [4]
- Silver nanoparticles (Ag NPs): higher sensitivity [2], [5] shape, size, surrounding dielectric [2], [6], [7]
- Spectra of aggregates parameters, N number, g distance, spatial distribution [8]
- Effect of the E-field oscillation direction Longitudinal modes: red-shift, transveral modes: blue-shift [9]
- Co-existence of modes: local intensity enhancement 5000* [10]
- Monitoring the shift: quantitative bio-detection [11]

2. METHODS AND MATERIALS

- Preparation of silver nanoparticles [12]
  Ag NP - Cys bioconjugates with 30:1 ratio
- TEM observation of Ag Nps
  size distribution: UTHSCSA Image tool 2.00 Software
- Experimental spectral study
  reactivity of the amino-groups => aggregation is pH dependent
- Ag NP - Cys bioconjugates
  investigated pH: 4.92 and 5.7
  Ocean Optics USB200: λ= 300-900 nm
- Computation of absorptance spectra by finite element method
  FEM, COMSOL (version 4.1)
  λ=300-900 nm, $\Delta\lambda$=10 nm + $\Delta\lambda$=1 nm surrounding the maxima

Purpose:
reproducing maxima observed on the spectra of Ag NP aggregates, explaining the origin of spectral peaks based on near-field study

Parameters:
d=8.25 +/- 0.05 nm, t= 0.45 nm,
n_{Ag} [13], n_{cys} [14,15], n_{water} [16]
- both the polar angle (φ) and the azimuthal angle (γ) are varied

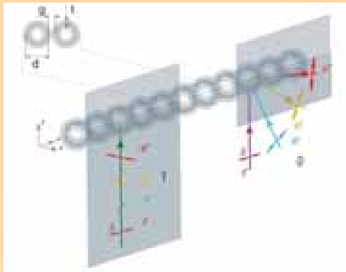


Figure 1. Schematic drawing of a linear Ag-Cys aggregate showing computations parameters.

N - number of Ag NPs
d - diameter of spheres
t - thickness of the Cys-shell
f - the distance between Ag NPs
g - gap between Ag NPs, g=f-d.
The colored arrows indicate the directions of polarized light illumination.

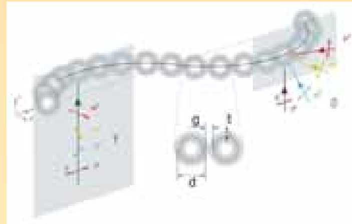


Figure 2. Schematic drawing of a 2D wavy aggregate showing all computation parameters.

3. RESULT AND DISCUSSION

Comparison of spectra on silver nano-particle-aggregates at pH = 4.92 and pH = 5.7

FWHM confirms the co-existence of versatile linear and 2D wavy chains of Ag Nps with different N, g parameters

pH 4.92

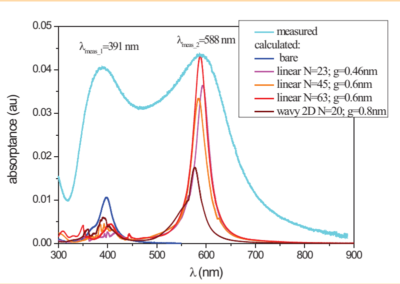
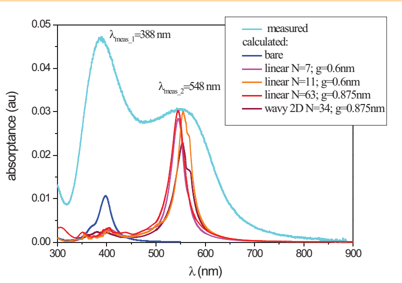


Figure 3. The absorptance spectra measured on Ag NP-Cys bioconjugates' solution at (a) pH=4.92 and (b) pH=5.7 (turquoise), and their absorptance spectra calculated by FEM for bare Ag NP (blue), three linear chain-like ensembles with different N, g parameters (pink, orange, red), and a 2D wavy aggregate (purple), which result in absorptance maxima surrounding the UV and red-shifted measured peaks. The two measured spectra are normalized to match the red peaks corresponding to their best fit.

pH 5.7



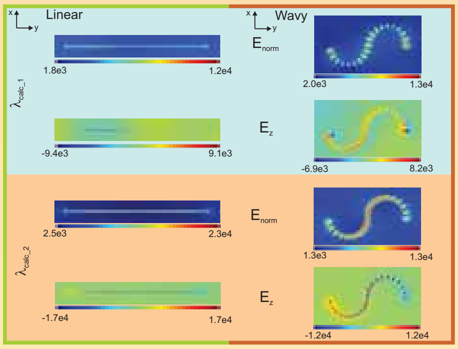
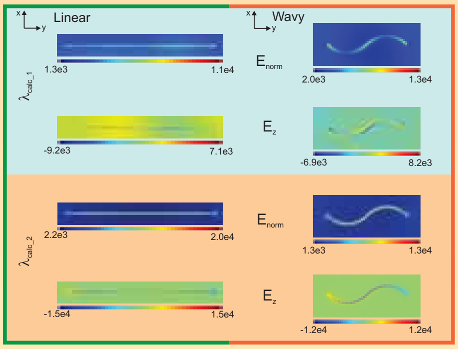


Figure 4. Electric-field distribution at the extrema measured in the UV: first two rows, and at the red-shifted peak: last two rows. First and third rows: the normalized electric field (E_{norm}) in XY plane; second and forth rows: the E_z component in XY plane along Ag NP chains, for linear chain-like aggregates (first column), and for ~sinusoidal 2D wavy aggregates (second column).

UV: quadrupolar

Red-shifted: dipolar



	N	f (nm)	g (nm)	Max1(nm)	Max2 (nm)	L(nm)	Split (nm)	FWHM(nm)
Single bare	1			398				
Lin calc	23	8,71	0,46	401	593	201	192	33
Lin calc	45	8,85	0,6	398	585	399	187	35
Lin calc	63	8,85	0,6	405	588	558	183	34
Sinusoidal	20	9,05	0,8	398	577	181	179	37
Measured pH 4,92				391	588	523	197	

	N	f (nm)	g (nm)	Max1 (nm)	Max2 (nm)	L(nm)	Split (nm)	FWHM (nm)
Single bare	1			398				
Linear I	7	8,85	0,6	401	545	62	144	31
Linear II	11	8,85	0,6	402	555	98	153	33
Linear III	63	9,125	0,875	403	545	575	142	33
Sinusoidal	34	9,125	0,875	386	554	310	168	40
Measured pH 5,7				388	548	431,7	160	

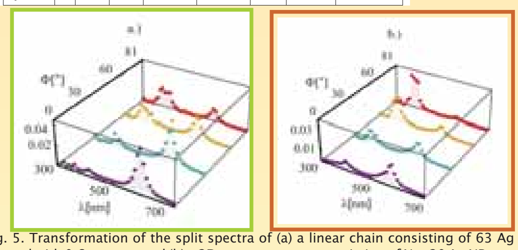


Fig. 5. Transformation of the split spectra of (a) a linear chain consisting of 63 Ag NPs arrayed with 0.6 nm gap, and (b) a 2D wavy aggregate consisting of N = 20 Ag NPs arrayed with g=0.8 nm gap, when the φ angle of incidence is increased from φ=0° resulting in dominantly longitudinal resonance corresponding to the red-shifted maximum, to φ =90° resulting in dominantly transversal resonance corresponding to the UV peak.

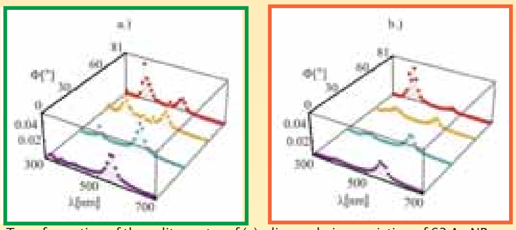


Fig. 7. Transformation of the split spectra of (a) a linear chain consisting of 63 Ag NPs arrayed with 0.875 nm gap, and (b) a 2D wavy aggregate consisting of N = 34 Ag NPs arrayed with g=0.875 nm gap, when the φ angle of incidence is increased from φ=0° resulting in dominantly longitudinal resonance corresponding to the red-shifted maximum, to φ =90° resulting in dominantly transversal resonance corresponding to the UV peak.

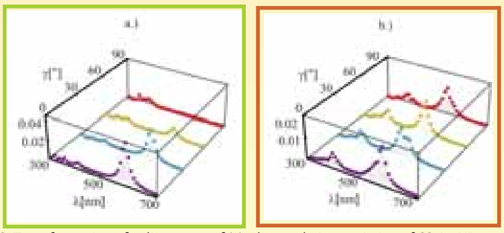


Fig. 6. Transformation of split spectra of (a) a linear chain consisting of 63 Ag NPs arrayed with 0.6 nm gap, and (b) a 2D wavy aggregate consisting of N=20 Ag NPs arrayed with g=0.8 nm gap, when the azimuthal orientation is tuned from γ=0° resulting in dominantly longitudinal resonance", to γ =90° resulting in entirely transversal resonance on the linear chain and a coexistent transversal and longitudinal resonances on the sinusoidal chain.

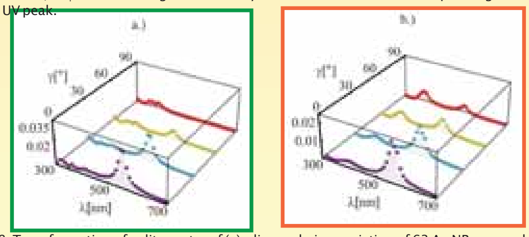


Fig. 8. Transformation of split spectra of (a) a linear chain consisting of 63 Ag NPs arrayed witht 0.875 nm gap, and (b) a 2D wavy aggregate consisting of N=34 Ag NPs arrayed with g=0.875nm gap, when the azimuthal orientation is tuned from γ=0° resulting in dominantly longitudinal resonance", to γ =90° resulting in entirely transversal resonance on the linear chain and a coexistent transversal and longitudinal resonances on the sinusoidal chain.

4. CONCLUSION

- aggregation of cystein functionalized Ag-NPs is pH dependent
- highest degree of aggregation at 4.92 pH
- highest pH resulting in aggregation: 5.7 pH
- split spectra with UV and red-shifted peaks

- Red-shifted peak:
  dipolar resonance originating from coupled dipoles

- UV peak:
  quadrupolar resonance on extended aggregates

- increase of the polar angle: partial/pronounced transformation from longitudinal (dipolar) to transversal (quadrupolar) resonance on linear/2D wavy aggregates

- increase of azimuthal angle: complete/partial transformation from longitudinal (dipolar) to transversal (quadrupolar) resonance on linear/2D wavy aggregates

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