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Off-Resonant Two-Photon Absorption Cross-Section Enhancement of an Organic Chromophore on Gold Nanorods

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Abstract

Surface-plasmon-initiated interference effects of polyelectrolyte-coated gold nanorods on the two-photon absorption of an organic chromophore were investigated. With polyelectrolyte bearing gold nanorods of 2,4,6 and 8 layers, the role of the plasmonic fields as function of distance on such effects was examined. An unusual distance dependence was found: enhancements in the two-photon cross-section were at a minimum at an intermediate distance, then rose again at a further distance. The observed values of enhancement were compared to theoretical predictions using finite element analysis and showed good agreement due to constructive and destructive interference effects.

Keywords

Plasmonics; two-photon absorption

Plasmonic electromagnetic effects define the linear and nonlinear optical (NLO) properties of confined metallic structures.^{1,2} For noble metals, these electric fields are induced by localized surface plasmon resonance (LSPR) frequencies in the visible part of the spectrum.³ Their amplitude and spectral response are a function of their dimensions, local environment and state of aggregation.⁴ Additionally the electric fields set up by the accumulation of charges at sharp edges and corners, termed the “lightning rod effect,” also contribute to the signal enhancement.⁵ Fascinating applications and phenomena that arise from these effects include novel devices for optical data storage^{6,7} and active control of the propagation of light for nano-photonics.⁸ An elegant demonstration by Zijlstra and coworkers showed that optical storage up to 7.2 terabits was possible with gold nanorods.⁹ With the premise of ultra-fast manipulation of data in the future, researchers have looked into understanding plasmonic nanomaterial NLO behavior using femtosecond spectroscopy.¹⁰ Depending on

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SUPPORTING INFORMATION AVAILABLE: Zeta potential measurements of the nanorods, chemical structure, emission and absorption spectra of the chromophore, one and two photon power scans. This material is available free of charge via the Internet <http://pubs.acs.org>.

the laser power and fluence, electron and lattice non-equilibrium effects contribute to the plasmonic optical nonlinearity.¹¹

Previously, various groups have demonstrated that for on-resonant excitation of the plasmon resonance frequencies, the nonlinearities that exist can be considered to be bulk-like with an additional plasmonic enhancement contribution in the far field.¹² Often overlooked is how such plasmonic nonlinearities occur within the near field. By describing the surface plasmon resonance as damped harmonic oscillations, Aussenegg and co-workers showed constructive and destructive interference effects for off-resonant two-photon excitations of lithographically patterned gold nanostructures.¹³

Based on these findings, the effect of off-resonant gold nanorod LSPR on the two-photon absorption (TPA) cross-section enhancement factor of a bound organic dye, AF348-3A, is examined herein. In a previous study from our group, the incoming laser excited both the two-photon absorbance of the AF348-3A chromophores and the LSPR of the gold nanorods to which they were bound.¹⁴ The TPA cross-section enhancement factor of the AF348-3A/gold nanorod system was found to be dependent on the dye-gold nanorod separation, with a maximum enhancement factor of 40 obtained at the closest distance; the TPA enhancement dropped off cleanly as a function of chromophore-nanorod distance.¹⁴ In the present study, AF348-3A was placed at variable distances from gold nanorod surfaces for nanorods in which the LSPR does *not* overlap the dye's TPA maximum. Using the method of Hermann and Ducuing,¹⁵ the dye's TPA cross-section at 800 nm was examined as a function of its spatial separation from the gold nanorod surface. This method has been previously demonstrated to give accurate TPA cross-section enhancement factors that are free of parasitic optical and photophysical effects that would yield an artificially high TPA enhancement factor.^{14,16}

Aspect ratio two (AR 2) gold nanorods were synthesized with an LSPR at approximately 650 nm using a previously reported procedure.¹⁷ The as-synthesized nanorods were stabilized by a positively-charged CTAB bilayer,¹⁸ onto which polyelectrolytes can be wrapped using layer-by-layer deposition.¹⁹ Previously, we have successfully demonstrated that it is possible to bind at variable distances the TPA chromophore AF348-3A to gold nanorods with polyacrylate (PAA) and polyallyamine hydrochloride (PAH) dielectric polyelectrolyte spacer layers.¹⁴ Figure 1 shows the experimental schematic of the gold nanorods with the attached chromophore molecules for 2, 4, 6 and 8 polyelectrolyte layer-bearing gold nanorods; this corresponds to spatial distances of 3, 6, 9 and 12 nm respectively.¹⁹

Electronic absorption spectra of the AF348-3A-bearing, 2, 4, 6, and 8 polyelectrolyte layer-coated gold nanorods are shown in Figure 2. Slight blue and red shifts in the absorption maxima are observed and are associated with the variable refractive index of the space surrounding the gold nanorods (*e.g.*, different degrees of polyelectrolyte hydration). Slight plasmonic broadening at ~800 nm suggests minor aggregation that we cannot eliminate completely. For each sequential polyelectrolyte assembly, zeta-potential measurements indicate the expected change in the effective surface charge (Figure S1) of the gold nanorods, suggesting that electrostatic, layer-by-layer self assembly is occurring. The absorption spectrum of AF348-3A is not observed in Figure 2 because the molar absorptivity of the longitudinal plasmon resonance of the gold nanorod is several orders of magnitude higher than that of AF348-3A.¹⁴

Nonlinear measurements were carried out in aqueous solutions (Millipore) with an absorbance of approximately 0.25 at the global absorption maximum. Measurements of the TPA cross-section enhancement factors were obtained using an instrument and technique previously described.¹⁴ Briefly, the 800 nm, 150 fs, 1000 Hz output of a Ti:Al₂O₃

regenerative amplifier (Spectra-Physics Hurricane) excited an aqueous solution of the neat dye or dye complexed to gold nanorods for measurement of the dye's two photon fluorescence. The 800 nm output of the laser was also doubled by way of a frequency doubling crystal to a frequency-equivalent wavelength of 400 nm. The sample was excited again and its one photon fluorescence spectrum obtained. The two-photon absorption cross-section of the neat dye or the dye complexed to gold nanorods was obtained the method of Hermann and Ducuing (Eq. 1).¹⁵ The ratio of the two-photon absorption cross-section of the gold nanorod-bound dye to that of the neat dye solution is defined as the two-photon absorption cross-section enhancement factor. Only this enhancement factor, and not the absolute cross-sections, will be reported. Our recent related work for the on-resonant case of a two-photon absorber on gold nanorods featured 200–1000 chromophores per rod.¹⁴

The calculation of the AF348-3A two-photon absorption cross-section, $\sigma^{(2)}$, is described by (Eq. 1), where $\sigma^{(1)}$ represents the linear, one photon, absorption cross-section, $\phi_{2\omega}$ is the one photon excitation power, ϕ_{ω} represents the two photon excitation power, and $I(2PL)$ and $I(1PL)$ are the two photon- and one photon-fluorescence intensities, respectively.¹⁵ Using (1) to calculate $\sigma^{(2)}$ has several advantages. The concentration of the dye on the gold nanorod is not precisely known; as a result, it is not possible to match the concentration of the neat dye solution to the dye concentration of the nanorod solution. To better ensure repeatability and to keep a uniform background level, matched optical densities were used instead. With Eq. 1, the ratio of the one- and two-photon fluorescence intensities, corrected for the excitation power, is calculated. This corrects for concentration differences and makes absolute knowledge of the dye concentration unnecessary. Additionally, by dividing by the pair of fluorescence intensities for each sample, other nonlinear and scattering effects of the gold nanorods are corrected for.

$$\sigma^{(2)} = \sigma^{(1)} \frac{\phi_{2\omega} I(2PL)}{\phi_{\omega}^2 I(1PL)} \quad (1)$$

The $\sigma^{(2)}$ measurement technique described in (1) works with only one pair of linear- and two photon-fluorescence intensities; however, a much more robust approach involves several sets of excitation and fluorescence intensities. Using the latter method has two main benefits. The first is that with several sets of intensities, a statistically meaningful set of data can be obtained. Secondly, the correct power law relationship for the fluorescence can be confirmed for the $\sigma^{(2)}$ measurement; for a plot of the one photon fluorescence intensity versus excitation energy density, the relationship should be linear with a slope of 1.0. For two photon fluorescence, the plot should be quadratic. Figures S4–S11 confirm that the correct excitation power laws are followed for the neat dye and dye-bound gold nanorod samples.

The $\sigma^{(2)}$ enhancement factors (Figure 3) for AF348-3A separated from a gold nanorod by two, four, six and eight layer samples are 8.08 ± 1.27 , 2.32 ± 0.38 , 3.26 ± 0.28 , and 9.28 ± 1.44 , respectively. Nominally, these distances would be 6, 9, 12 and 15 nm from the metal surface assuming a 3 nm CTAB bilayer and 1.5 nm per subsequent polyelectrolyte layer. The distance dependence of the two-photon absorbance cross-section shows an unusual, unexpected pattern: the $\sigma^{(2)}$ enhancement decreases by a factor of almost four then increases by the same amount as the dyes are further from the nanorod surface. This is in complete contrast to the same experiment performed when both LSPR and chromophore TPA are excited together: that result shows that two polyelectrolyte spacer layers have a 40-fold enhancement which exponentially drops off, as the number of spacer layers increases.¹⁴ The error bars reflect batch-to-batch variability and some slight degree of aggregation; the error

bars are similar to those observed in our previous work for the on-resonant two-photon case.¹⁴

Aussenegg and co-workers examined a related situation using lithographically-prepared gold nanorods with femtosecond third harmonic generation (THG) techniques.¹³ Two sets of data were obtained: one for gold nanorods whose LSPR was at the wavelength of the laser (the resonant case) and a second when the LSPR was shifted away from the laser's wavelength (the off-resonant case). It was found that the resonant case showed a smooth envelope of THG intensity as a function of delay time, corresponding to calculated electric field oscillations that were in phase with the laser pulse field. But the off-resonant gold nanorod case featured beating, in which the calculated electric field oscillations were out of phase with the laser pulse field. This beating can be attributed to a mixture of constructive and destructive interference. The gold nanorod samples will partially reflect and scatter the incident laser pulse; a surface plasmon generated by this laser pulse will have an electric field that extends into the space surrounding it. Depending on the distance from the gold nanorod, the electric field of the back-scattered or back-reflected laser pulse will show either constructive or destructive interference with the localized surface plasmon's electric field. In Figure 3, if the distance of the AF348-3A molecule from the gold nanorod lies in a region of constructive interference, a higher $\sigma^{(2)}$ enhancement factor will be observed. If the dye molecule is in a region of destructive interference, the $\sigma^{(2)}$ enhancement factor will decrease.

Finite element method simulations using COMSOL Multiphysics were used to explore the unusual measured $\sigma^{(2)}$ enhancement pattern. The rate of excitation, R , for a molecule can be described using Eq. 2 for one- and two-photon excitations, where N is the number density of the absorbing species, σ is the cross section, and I is the light intensity of the exciting wavelength, λ .²⁰

$$R = N\sigma^{(1)}f^2(\lambda_i)I(\lambda_i) + N\sigma^{(2)}f^4(\lambda_i)I^2(\lambda_i) \quad (2)$$

The local field factor, f , represents the sensitivity of the absorption mechanism to an increase in the electric field experienced by a molecule. For a two-photon absorption process, $\sigma^{(2)}$ increases proportionally to the fourth power of the electric field. Using the electric field calculated in COMSOL, the electric-field ratio, normalized to the 8-layer case, can be calculated using Eq. 3. Details of the simulation can be found elsewhere.¹⁴

$$Ratio = \frac{(Electric\ field\ at\ x\ layers)^4}{(Electric\ field\ at\ 8\ layers)^4} \quad (3)$$

The calculated electric field to the fourth power for the two-, four-, six-, and eight-layer samples is divided by the electric field to the fourth power for the eight layer sample. A plot of the electric field ratio versus the number of layers can be found in Figure 4. The calculated electric field ratio follows the same pattern found in the measured $\sigma^{(2)}$ enhancement factors (the red line in Figure 3): a slight decrease, followed by an increase, is observed. The measured $\sigma^{(2)}$ enhancement factors are normalized to the calculated $\sigma^{(2)}$ enhancement factor at eight layers (Table 1). Within the standard deviation of the measured $\sigma^{(2)}$ enhancement factors, their ratios exhibit quantitative agreement with the calculated ratios, indicating that the interference model described by Aussenegg et al.¹³ may be a valid description for the measured $\sigma^{(2)}$ enhancement factors. The chosen range of polyelectrolyte layers lies in the tail of the electric field interference pattern, and as the thickness approaches 8 layers and beyond, the maximum of the plasmon electric field is approached, giving rise to the observed enhancement pattern.

Our studies indicate that the plasmonic-induced interference effects of gold nanorods on NLO properties of bound chromophores can be observed if chromophores are positioned to sample the local electronic fields. By accounting for scattering and absorption effects in our enhancement of TPA using the Herman and Ducuing method, we observe such effects are pronounced at distances of approximately 3–15 nm from the surface of the nanoparticles. Recent work in the literature shows other fascinating effects, both experimental and theoretical, of plasmons on molecules.^{21,22} We envision understanding these effects will be of great value to fabricating plasmonic NLO devices of the future.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Cartoon of a polyelectrolyte-coated gold nanorod with the AF-348-3A chromophore. Gold bar: gold nanorod. Dashed line: A polyelectrolyte spacer layer of thickness d that separates the gold surface from the chromophore. Green stars: AF-348-3A chromophore (inset shows chemical structure). Redline : Polyelectrolyte trap coat layer.

Figure 2. Normalized electronic absorption spectra of gold nanorods of aspect ratio two in water, bearing two (black), four (red), six (blue), eight (pink) polyelectrolyte spacer layers between the gold nanorod surface and the AF348-3A chromophores, in all cases followed by a PAA trap coat. The blue vertical dashed line represents the maximum two-photon absorption wavelength of AF348-3A.

Figure 3.

Measured two-photon absorption cross-section enhancement (left axis, black points) and the calculated electric field ratio of layer n to layer 8 (right axis, red points) for AR 2 polyelectrolyte-bearing gold nanorods complexed with the AF348-3A chromophore, as a function of number of spacer layers. The red line is drawn only to aid the eye.

Figure 4.

Electric field ratio of AR 2 gold nanorods, for layer n divided by layer 8, calculated using COMSOL Multiphysics for different refractive indices n : ■, $n = 1.3$; ●, $n = 1.4$; ▲, $n = 1.5$; ▼, $n = 1.6$; ◆, $n = 1.7$.

Table 1

Measured and calculated two photon absorption cross-section enhancement ratios for the off-resonant plasmon case, normalized to the 8-layer case.

Number of Layers	Calculated Ratio [*]	Measured Ratio
2	0.60	1.06 ± 0.85
4	0.47	0.34 ± 0.26
6	0.63	0.48 ± 0.19
8	1	1

^{*}
for $n = 1.5$