

Dispersed and Encapsulated Gain Medium in Plasmonic Nanoparticles: a Multipronged Approach to Mitigate Optical Losses

Antonio De Luca,^{†,*} Marcin P. Grzelczak,[‡] Isabel Pastoriza-Santos,[‡] Luis M. Liz-Marzán,[‡] Massimo La Deda,[§] Marinella Striccoli,[⊥] and Giuseppe Strangi[†]

[†]CNR-IPCF Licryl Cosenza, Department of Physics - University of Calabria, 87036 Rende, Italy, [‡]Departamento de Química Física and Unidad Asociada CISC - Universidade de Vigo, 36310 Vigo, Spain, [§]Department of Pharmaceutical Sciences, and CEMIF.CAL, 87036 Rende (CS), Italy, and [⊥]CRN-IPCF Bari-c/o Department of Chemistry, Via Orabona 4, 70126 Bari, Italy

The problem of optical loss in metastructures based on metal subunits represents a central topic that has to be tackled before we can move toward the fabrication of metamaterials in the visible range because most of the extraordinary electromagnetic properties expected in nanostructured systems are shadowed by unavoidable absorptive effects. Recently, theoretical studies have shown that bringing gain in proximity to metal subunits can reduce the strong radiation damping, in terms of reduction of the imaginary part of the dielectric permittivity.¹ This would enable promising new applications of these materials in fields such as materials science,² biophysics,³ molecular electronics, and fluorescence spectral engineering based on surface-enhancement effects.⁴ Compensation of the strong losses caused by metal absorption would permit us to operate at optical frequencies, opening the possibility to investigate phenomena such as perfect lenses,⁵ cloaking,^{6,7} and others not yet conceived. A recent experimental work performed on plasmonic structures with gain units dissolved in solution⁸ showed that the presence of fluorescent molecules in a mixture may modify the scattering intensity as a function of the gain owing to the enhancement of the quality factor of surface plasmon resonances (SPRs). It is well-known that relevant modifications of the fluorescence of dye molecules placed in close proximity to metal nanoparticles (NPs) are due to mutual interactions with nanoparticle surface plasmons (SPs), including resonant energy transfer.^{9–11} A localized SP represents a collective oscillation

ABSTRACT The performance of all metamaterial-based applications is significantly limited by the inherent and strong energy dissipation present in metals, especially in the visible range. In fact, these materials suffer from rather strong damping of the plasmon fields which can become obstructive for most optical and photonic applications. Therefore, eliminating losses in optical metamaterials is critical for enabling their numerous potential applications. We experimentally demonstrate that the incorporation of gain material (fluorophores) in the high-local-field areas of a metamaterial subunits (gold core/silica shell nanoparticles) makes it possible to induce resonant energy transfer processes from gain units to plasmonic nanoparticles. A comparison between gain-assisted (nanoparticle–dye dispersion) and gain-functionalized (dye encapsulated into the shell) systems is reported. Fluorescence quenching and time-resolved spectroscopy along with modification of Rayleigh scattering and transmission of a probe beam as a function of impinging energy are key evidence of the strong coupling occurring between NPs and gain medium. The multipronged approach used to compensate losses in these metal-based subunits permits one to obtain important advances in materials science and paves the way toward further promising scientific research aimed to enable the wide range of electromagnetic properties of optical metamaterials.

KEYWORDS: plasmonic nanoparticles · loss compensation · metamaterials · functionalized gain media · resonant energy transfer

of electron charges in metallic nanoparticles, whose resonance frequency (LSPR frequency) is sensitive to dielectric changes of the environment, as well as to the size and shape of the nanoparticle. A phenomenon relevant to localized SPs is a surface plasmon polariton (SPP), that is, a surface electromagnetic wave propagating parallel to the interface between two media possessing permittivities with opposite signs, such as a metal and a dielectric. In both cases, oscillations are excited by light, exhibiting enhanced near-field amplitude at the resonance wavelength. Localized SPs have been found on rough surfaces,^{12,13} in engineered nanostructures,^{14–17} as well as in clusters

* Address correspondence to antonio.deluca@fis.unical.it.

Received for review April 28, 2011 and accepted June 17, 2011.

Published online June 17, 2011
10.1021/nn2015562

© 2011 American Chemical Society

and aggregates of nanoparticles (NPs).^{18–20} In 1989, Sudarkin and Demkovich²¹ suggested to increase the propagation length of a SPP by utilizing the population inversion created in the dielectric medium adjacent to the metallic film. Recently, gain-assisted propagation of SPPs at the interface between a metal and a dielectric with optical gain has been analyzed theoretically.^{22,23} The enhancement of the SPP at the interface between the silver film and the dielectric medium with optical gain (laser dye) has been recently demonstrated in ref 24 and described by Noginov for Ag aggregates in solution.⁸ Furthermore, a relevant phenomenon of SP amplification by stimulated emission of radiation (SPASER), based on Förster-like energy transfer from excited molecules to resonating metallic nanostructures introduced by Stockman *et al.* in 2003,^{25,26} has been theoretically analyzed by Zheludev *et al.*²⁷ and experimentally demonstrated in ref 28. At the same time, theoretical self-consistent calculation on gain-assisted metamaterials was proposed in 2009 by Fang *et al.*,¹ showing that 2D dispersive metamaterial losses can be compensated ($\text{Im}(\epsilon) = 0$), whereas both positive and negative values of $\text{Re}(\epsilon)$ can be obtained. Nevertheless, most of these studies have been performed in “gain-assisted” systems, where striking plasmonic properties have been evidenced, but the unavoidable problem of absorptive losses still requires many technical and scientific problems to be solved. Here, we report experimental studies aimed to demonstrate effective chemical and physical approaches to mitigate the absorptive loss effect by means of either gain-assisted (G_A) or gain-functionalized (G_F) core–shell metal nanospheres, selected as metamaterial building blocks. The main difference between these two approaches is that in the gain-assisted system fluorescent guest molecules are included in the designed structure by mixing them in solution with the plasmonic nanoparticles, whereas NP gain functionalization comprises “smart nanoparticles” carrying built-in gain elements compensating internal losses, obtained by incorporating optically active components (quantum dots or organic dyes) within the silica shell.

RESULTS AND DISCUSSION

The study was performed by investigating primarily the photophysical properties of adequate composites, dye–NP solutions, to evaluate the main parameters in resonant energy transfer mechanisms. Subsequently, gain-functionalized composites were considered, whose electromagnetic properties were modeled taking into account the presence of gain elements that can shift plasmonic resonances modifying the frequency response of the material. In particular, the effective rate of (nonradiative) excitation energy transfer from fluorescent dye molecules to surface plasmon

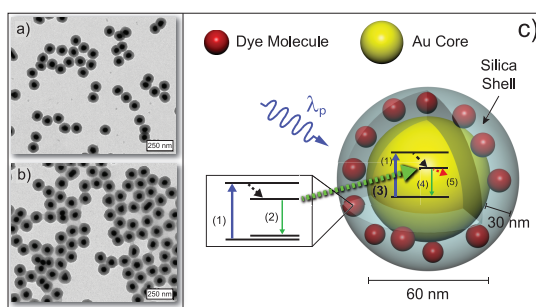


Figure 1. (a) TEM image of the gold core/silica shell NPs. (b) TEM image of the gain-functionalized system (Au@(SiO₂ + R6G)), with R6G incorporated within the silica shell. (c) Sketch of the nonradiative energy transfer process (green dashed line (3)) occurring from fluorescent dye molecules (red spheres, inside the silica shell of about 30 nm) to surface plasmon modes of properly functionalized gold cores (yellow sphere, $d \sim 60$ nm). The p is the pump wavelength, (1) is excitation; (2) dye radiative de-excitation; (3) nonradiative energy transfer; (4) plasmon state de-excitation; (5) thermal de-excitation (electron–phonon coupling).

modes of functionalized gold core/silica shell NPs has been investigated by exploiting a surface coating approach (see Figure 1).

The predicted behavior of the nonradiative transfer rate due to the Coulombic interactions²⁹ and a non-trivial nanoparticle size dependence represent key parameters to properly include gain units and provide effective gain to plasmonic elements. Therefore, a multipronged synthetic strategy was followed to bring the required functionalities at the plasmonic NPs acting as low-loss nanoresonators. The first step involved the dissolution of organic dyes in the NP dispersion to optimize compatibility, spectral overlap, and nonradiative transfer rate (gain-assisted approach), then this system was compared to the G_F system where the selected fluorescent molecules were encapsulated within the silica shell surrounding the noble metal NPs. More in detail, gain-functionalized metal nanoparticles consist of a gold core (diameter $d \sim 60$ nm) coated with a silica shell (30 nm thick) containing organic dye molecules (Figure 1).^{30–34} The photostable organic dye [Rhodamine 6G (R6G)] was optically excited by laser pulses at 355 nm, showing that its gain curve overlaps the plasmon band of gold NPs in both systems: gain-assisted (G_A) and gain-functionalized (G_F) (Figure 2).

Gain-Assisted (G_A) Gold Nanoparticles. Au core/silica shell nanospheres (core diameter 60 nm, silica shell 30 nm) were dispersed in an ethanol solution of R6G (0.01 wt %). Fluorescence spectroscopy allowed us to gain an understanding about the coupling between active dyes and plasmonic nanospheres. As observed by Dulkeith,³⁵ if a donor fluorescent molecule is maintained in the vicinity of a metal nanoparticle, a drastic quenching of fluorescence is expected. This effect was predicted by Gersten and Nitzan by considering a

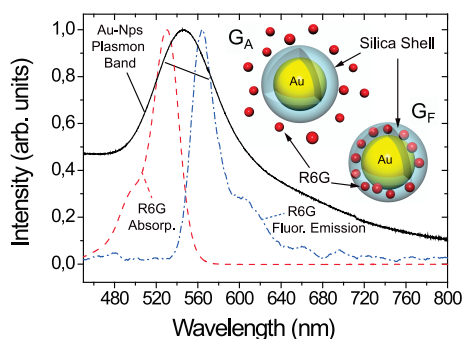


Figure 2. Absorption (dashed line) and emission (dash-dot-dot line) spectrum of Rhodamine 6G dye in ethanol and plasmon bands of gain-“assisted” and gain-“functionalized” gold nanoparticles. (G_A) Sketch of the gain-assisted system ($\text{Au@SiO}_2/\text{R6G}$) in which R6G dye molecules have been dissolved in the ethanol solution of gold core/silica shell NPs; (G_F) R6G has been encapsulated within the silica shell (dotted line).

remarkable enhancement of nonradiative resonant energy transfer between donor fluorophore and plasmonic acceptor.⁹ Inset of Figure 3 shows the fluorescence quenching observed in the $\text{Au@SiO}_2/\text{R6G}$ system with respect to the pure R6G ethanol-based solution (same concentration, 0.01 wt %) when optically pumped with large spotted pulse trains of a tripled Nd:YAG laser ($\lambda = 355$ nm) at the same pump energy.

By plotting the maximum fluorescence emission as a function of pump energy for both solutions (Figure 3), a different rate was observed. This can be the consequence of resonant nonradiative energy transfer process occurring from gain molecules to metal units present in the surrounding volume, which causes the decrease of the radiative rate. Indeed, upon studying fluorescence changes in these gain-assisted systems, only fundamental indications of excitation energy transfer processes can be obtained. These observations are necessary but not sufficient to demonstrate mitigation of absorptive losses. Hence, time-resolved fluorescence spectroscopy along with pump–probe experiments has been carried out on both gain-assisted and gain-functionalized systems to perform a comparative analysis of gain-induced optical loss modifications.

Gain-Functionalized (G_F) Gold Nanoparticles. The step forward is represented by the functionalization of core–shell NPs by encapsulating properly selected fluorescent guest molecules within the silica shell to induce effective resonant energy transfer in dye-doped meta-structures. As compared to the gain-assisted system, this approach allows a fine control of key parameters such as dye–metal core interdistance and dye concentration, offering the advantage of clearing inactive fluorescent molecules from solution and allowing one to maintain almost unmodified the energy density of the optical pump. In this framework, material parameters of core–shell NPs have not been modified, the difference only being the encapsulation of R6G dye molecules within the shell. This process allows us to bring

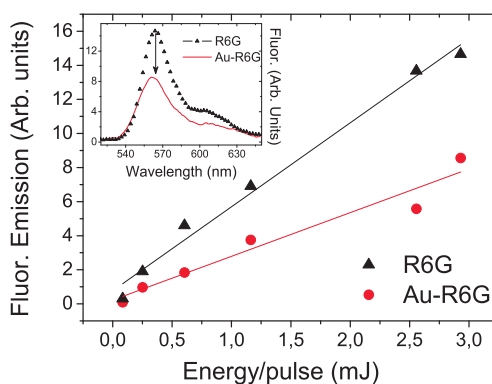


Figure 3. Inset: Fluorescence quenching observed in G_A (black triangles) with respect to the R6G ethanol-based solution (solid red line) under the same pump energy value. Fluorescence emission maxima of the gain-assisted sample (red circles) with respect to the R6G ethanol-based solution (black triangles) as a function of pump energy ($\lambda = 355$ nm).

gain to single gold nanoparticles, which can overcome direct energy feeding through nonradiative mechanisms.

Fluorescence lifetime measurements demonstrate fluorescence quenching behavior, consistent with a small separation distance from dyes to the surface of the nanoparticle because of their strong resonant coupling. Figure 4 reports the time-correlated single-photon counting (TCSPC) data at 560 nm for G_A and G_F systems with respect to the pure R6G dye solution when irradiated with a 265 nm NanoLed pulsed laser diode. The time-resolved fluorescence intensity decay of the ethanol solution of pure R6G molecules is fitted as a single-exponential function in Figure 4 (red dots and green line fit), giving a time constant of $\tau_{\text{Fluo}} = R_{\text{Fluo}}^{-1} = 5.4$ ns ($\chi^2 = 0.978$). From the TCSPC data of the gain-assisted system (blue dots and cyan line fit), two components can be identified in the decay dynamics. A fast decay (of $\tau_{A1} \sim 190$ ps; $\chi^2 = 0.978$, Figure 4b) is accompanied by a long-living emission where the decay kinetics resembles the fluorescence decay for pure R6G dye molecules. The first decay time is attributed to the fraction of dye molecules decorating the silica shell that experience the resonant energy transfer process; the long-living emission is related to the fraction of unbound dye molecules (the largest fraction) present in solution but that are not coupled to plasmonic nanoparticles. Strikingly, the time-resolved spectrum of the G_F system (pink dots) shows only a short-living intensity emission decay, fitted as a single-exponential with a time constant $\tau_F \sim 120$ ps ($\chi^2 = 1.058$). Accordingly, this decay time can be attributed to the encapsulated fluorescent molecules resonantly coupled to the plasmonic gold core. It is worth noting that in the G_F system we have not measured long-living emission due to unbound R6G molecules. Thus, the identification of a single-exponential decay of the short-living encapsulated dye emission indicates a complete and effective dye–NP coupling, which is manifested as a

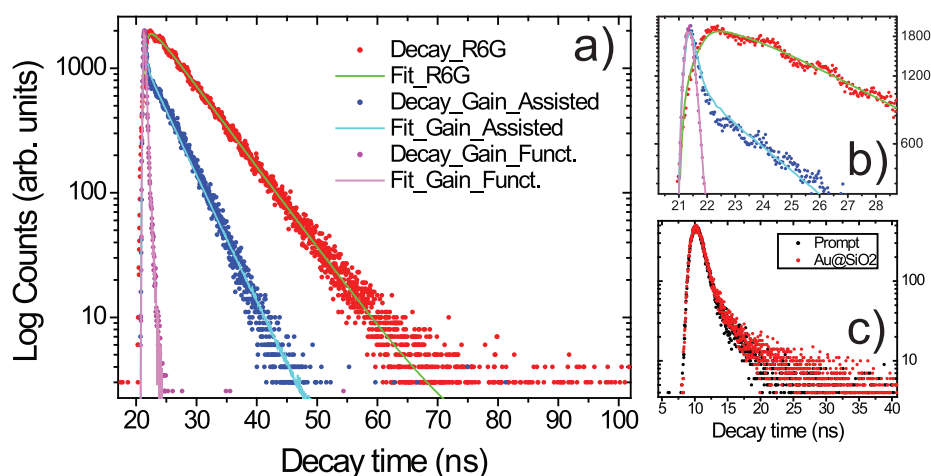


Figure 4. (a) Time-resolved fluorescence intensity decays: G_A and G_F systems are compared to pure R6G dye solution. Long-living emission of pure R6G characterized by a time constant $\tau_{\text{Fluo}} = 5.4$ ns (red dots). Two components are identified in the decay dynamics of the G_A system: $\tau_{A1} \sim 190$ ps and $\tau_{A2} \sim 6.0$ ns (blue dots). A short-living emission is identified for G_F ($\tau_F \sim 120$ ps), clearly indicating a strong dye–NP coupling. (b) Zoom image of the time-resolved fluorescence decays in the first 7 ns. The double decay time in the case of the G_A system is more evident. (c) TCSPC data collected from a solution containing the Au@SiO₂ particles only; results obtained in the same experimental conditions as used for the G_F system confirm that the origin of short decay is due to the dye–NP coupling.

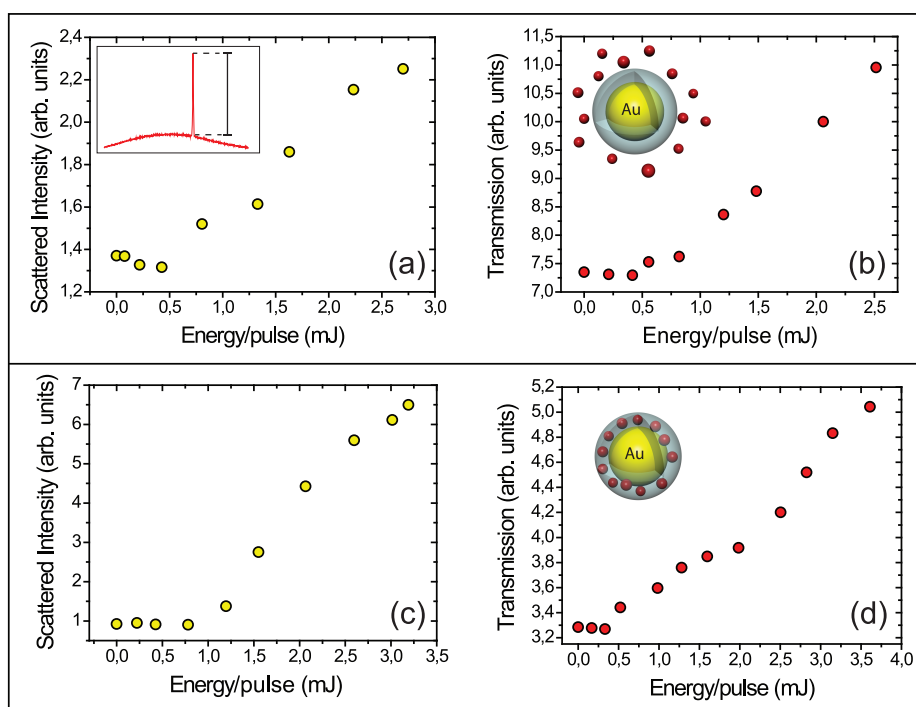


Figure 5. Comparison of scattering and transmission enhancement signals between gain-assisted (a,b) and gain-functionalized (c,d) samples. Enhancement of SP evidenced by an increasing of normalized Rayleigh scattering signal of probe beam as function of pump energy (355 nm) for (a) Au@SiO₂/R6G and (c) Au@(SiO₂ + R6G) samples. Normalized transmission increasing of a probe beam at 532 nm as a function of pump energy for (b) Au@SiO₂/R6G and (d) Au@(SiO₂ + R6G) samples. Comparable threshold values for both transmission and scattering signals have been observed in the two samples.

significant reduction of the radiative rate. To exclude a possible interference caused by the presence of Au@SiO₂ particles, TCSPC data have been collected from a solution containing the Au@SiO₂ particles only; the results obtained in the same experimental conditions as used for the G_F system are clearly different, confirming that the origin of the G_F system short decay is due to the dye–NP coupling (Figure 4c). All of these

results elucidate the nonradiative energy transfer rate as a consequence of strong coupling for the G_F system. According to Beer–Lambert–Bouguer law, by measuring simultaneously Rayleigh scattering and transmission, either in the absence or in the presence of gain, we should be able to understand if the absorptive power of the material is affected by excitation energy transfer. Thus, modifications of Rayleigh scattering and

transmitted intensity of a constant probe beam ($\lambda = 532$ nm) have been monitored as a function of the pump energy for both systems (excitation @ 355 nm). As first proposed by Lawandy,³⁶ the localized SP resonance in metallic nanospheres is predicted to exhibit a singularity when the surrounding dielectric medium has a critical value of optical gain. This can be evidenced by an increase of the Rayleigh scattering signal because of the enhancement of the local field surrounding the nanoparticle. Hence, a pump–probe Rayleigh scattering experiment enables observation of the enhancement of the SP resonance due to the gain material present in the solution or chemically encapsulated in the silica shell surrounding the gold core. Pump–probe Rayleigh scattering experiments were performed by a colinear launch of a probe beam in a small portion of the volume excited by a wider pump spot at $\lambda = 355$ nm. The scattered probe light, acquired by means of the optical fiber of a high-resolution spectrometer, was observed in the spectrum as a relatively narrow line centered at 532 nm, on the side of a much broader emission band relative to the dye fluorescence (see inset of Figure 5a).

Thus, it could be easily separated from the dye emission. The difference between the maximum of the scattered beam and the corresponding value in the fluorescence emission spectrum is plotted as a function of the pump energy. Figure 5a shows the enhancement of Rayleigh scattering signal as a function of excitation energy in system G_A . The superlinear increase of the scattered signal above a certain threshold value of gain is a demonstration of the enhancement of the quality factor of SP resonance mediated by resonant energy transfer processes between active elements and gold cores within the composite NPs. The presence of a threshold gain value above which systems show a nonlinear behavior was already discussed by Lawandy,³⁶ arguing that a singularity in the NP local field is expected as the transferred energy compensates the absorptive losses by exciting NP surface plasmon modes. However, the key experiment of this work was performed by measuring the transmission at far field of probe lightwaves after passing the excited area with different level of gain, selected by varying the pump rate. Figure 5b shows the increase of transmission peaks of the probe signal as a function of the excitation energy, evidencing a clear gain-induced increase of the whole system transparency. The measured transmitted signal is only relative to the probe beam wavelength, selected by pinhole and notch

filters, since stray light checks ruled out any other undesired contribution. A comparative set of measurements (both scattering and transmission) have been performed also on the system G_F , revealing similar threshold values with respect to NP–dye solution, even if the total amount of present gain units was considerably reduced with respect to the G_A system. We plotted in Figure 5c the enhancement of Rayleigh scattering intensity at the probe wavelength (probe = 532 nm), as a function of the pump rate in the Au@(SiO₂ + R6G) sample. A pump energy threshold value of about 1 mJ/pulse represents clear evidence that the amount of gain molecules, now encapsulated in the shell (10^3 – 10^4 molecules, by considering a few percent of occupied volume ratio), was sufficient to permit an effective nonradiative energy transfer to gold NPs and promote excitation of the surface plasmon modes, by providing an estimated local gain of about 10^4 – 10^5 cm⁻¹.³⁶ This effect can be explained by considering the interdistance dependence of the energy transfer rate,³⁷ owing to NP–dye dipolar interactions according to Förster theory.²⁹ Figure 5d shows that the transmission of light with wavelength selected within the resonant band and propagating through the excited volume experienced a considerable enhancement as the gain was increased. A critical behavior of the transmission was observed above a given threshold value of about 0.33 mJ/pulse, revealing that a reduction of optical absorption can be induced only if enough gain is provided. The gain-induced increase of optical transparency of meta-subunits becomes clearer when corroborated by experimental evidence which provides both direct measurements of the physical quantity (transmission) and effects clearly related to the energy transfer process (fluorescence quenching and Rayleigh scattering enhancement).

CONCLUSIONS

In conclusion, bringing gain to strongly absorptive meta-subunits can reduce the strong optical losses, either by gain-assisted nanoparticles through proper incorporation of gain molecules in structuring matrices or by functionalizing the single nanoparticle with gain units. We therefore demonstrated the possibility to fabricate metamaterials where gain media can be adequately inserted at different scale levels, ranging from the nanoscale to the macroscopic scale. Therefore, these results are of particular importance to move metamaterials from fundamental scientific challenges to applied materials.

METHODS

Chemicals. Ascorbic acid, tetraethylorthosilicate (TEOS), Rhodamine 6G, and NH₄OH (29%) were supplied by Aldrich.

Sodium citrate, HAuCl₄ × 3H₂O, and cetyltrimethylammonium bromide (CTAB) were purchased by Sigma. O-[2-(3-Mercaptopropionylamino)ethyl]-O'-methylpoly(ethylene glycol)

(mPEG-SH, M_w 5000) was procured from Fluka. Pure-grade ethanol and Milli-Q-grade water were used in all preparations. Synthesis of Au spheres: Au spherical particles with an average diameter of 58 ± 3 nm were prepared following the method developed by Rodríguez-Fernández *et al.*³² Briefly, 2.5 mL of ascorbic acid (0.5 mM) was added to 500 mL of an aqueous solution containing HAuCl₄ (0.25 mM) and CTAB (0.015 M) at 35 °C. Subsequently, the seed solution (15 nm citrate Au seeds, [Au] = 3.97×10^{-6} M) was added and allowed to react for 1 h.

Silica Coating. The Au nanoparticles were coated with silica using the method reported in ref 31. The 58 nm Au nanoparticles were first functionalized with mPEG-SH and transferred to ethanol. This was carried out by dropwise addition of an aqueous solution containing 1.06×10^{-6} mol of mPEG-SH to 5 mL of as-synthesized Au spheres (0.5 mM). After 30 min, the mixture was centrifuged (3300 rpm, 30 min) three times to remove excess mPEG-SH and redispersed in 3 mL of ethanol. The modified particles were then mixed with TEOS and ammonia in the following final concentrations: [Au] = 0.4 mM, [H₂O] = 10.55 M, [NH₃] = 0.2 M, [TEOS] = 0.8 mM. The thickness of silica shell after this first growth step was around 19 nm. Before a second growth step, the sample was centrifuged (3100 rpm for 30 min) to remove any free silica nuclei. Eventually, the silica shell was overgrown up to 30 nm by adjusting the concentration of silica precursors as indicated above. Some of the obtained core/shell NPs were added to an ethanol-based solution of Rhodamine 6G dye at a concentration of 0.01 wt % and a weight ratio of 9.5:1 with respect to NPs. The final system constitutes the Au@SiO₂/R6G sample.

Silica Coating in the Presence of Organic Dyes (Rhodamine 6G). The encapsulation of fluorophore probes was carried out by simply adding the dye (diluted in ethanol) dropwise under gentle stirring immediately prior to TEOS addition.³¹ The concentration of Rhodamine 6G in the reaction mixture was around 6 μM. The final system is represented by Au@SiO₂ + R6G, with R6G dye encapsulated into the silica shell.

Characterization and Measurements. Transmission electron microscopy (TEM) was carried out with a JEOL JEM 1010 transmission electron microscope operating at an acceleration voltage of 100 kV. The particles' size and shell thickness distributions were determined from TEM images using at least 100 particles. Fluorescence confocal microscope images were acquired on the prepared system Au@SiO₂/R6G (by a Leica TCS SP2, not shown here), aimed to study the dye–NP aggregation size and separation distance dependence in a resonant energy transfer process. These images, combined with SEM (Environment Quanta FEG 400 by Philips) and TEM observations of the same area, demonstrated that some metal aggregates appear in the solution, and that the dye is present in close proximity to these aggregates. This important observation confirms the possibility to activate Förster nonradiative energy transfer mediated by Coulombic interactions, even if the dye is dissolved in solution, toward the mesoscale building of metamaterials. On the other hand, to investigate the different nonradiative energy transfer rate as a consequence of diverse coupling strengths for G_A and G_F systems, the fluorescence lifetime of the two systems was acquired with respect to the pure dye solution, by means of a time-resolved spectrofluorometer (pump at 265 nm of a NanoLed pulsed laser diode, emission at 560 nm, HORIBA Jobin-Yvon Fluorolog-3 FL3-211), using the time-correlated single-photon counting (TCSPC) option. Excitation sources were mounted directly on the sample chamber at 90° to a single-grating emission monochromator (2.1 nm/mm dispersion; 1200 grooves/mm) and collected with a TBX-04-D single-photon-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH Data Station Hub photon counting module, and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). Goodness of fit was assessed by minimizing the reduced χ^2 function) and visual inspection of the weighted residuals. It resulted in the presence of two distinct decay times in the case of the G_A system, one related to the dye molecules experiencing the strong coupling with the metal NPs, the second one to the greater amount of gain molecules that do

not participate in the process. A shorter fluorescence lifetime (order of hundreds of picoseconds) was obtained in the case of the G_F system, indicating a more effective dye–NP coupling manifested as a relevant radiative rate reduction. Furthermore, Förster nonradiative energy transfer processes necessary to mitigate the high metal losses can be observed through indirect experiments. All of them are based on a pump–probe setup. The sample is optically pumped with 4 ns pulses of a third harmonic Nd:YAG laser (Brio by Quantel), $\lambda = 355$ nm. A probe beam (diode-pumped solid-state laser at 532 nm by Laser Quantum), with a fixed power, was focused within the pumped region of the sample. The probe wavelength was chosen in the proximity of the overlapping region between dye fluorescence and plasmon band maxima, where localized surface plasmon modes are expected. The probe light emitted, scattered, or transmitted by Au NPs ($\lambda = 532$ nm) was collected by an optical fiber together with the emission of dye, in a position depending on the particular experiment. The fiber was positioned at the angle of 70° relative to the beam propagation direction for scattering (90° for fluorescence) experiment, within several millimeters from the cuvette; transmission signals were acquired far from the sample, on the same pump beam direction and with a high neutral filter in front of the fiber head, in order to prevent any possible signal different from the probe one (high stable power).

Acknowledgment. The authors thank C. Versace, N. Scaramuzza, and A. Guerrero-Martínez for the fruitful scientific discussions. The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2008) Metachem Project under Grant Agreement No. 228762.

REFERENCES AND NOTES

- Fang, A.; Koschny, T.; Wegener, M.; Soukoulis, C. M. Self-Consistent Calculation of Meta-Materials with Gain. *Phys. Rev. B* **2009**, *79*, 241104.
- Imahori, H.; Fukuzumi, S. Porphyrin Monolayer-Modified Gold Clusters as Photoactive Materials. *Adv. Mater.* **2001**, *13*, 1197–1199.
- Powell, R. D.; Halsey, C. M. R.; Spector, D. L.; Kaurin, S. L.; McCann, J.; Hainfeld, J. F. A Covalent Fluorescent-Gold Immunoprobe: Simultaneous Detection of a Pre-mRNA Splicing Factor by Light and Electron Microscopy. *Histochem. Cytochem.* **1997**, *45*, 947–956.
- Lakowicz, J. R. Radiative Decay Engineering: Biophysical and Biomedical Applications. *Anal. Biochem.* **2001**, *298*, 1–24.
- Pendry, J. B. Negative Refraction Makes a Perfect Lens. *Phys. Rev. Lett.* **2000**, *85*, 3966–3969.
- Schurig, D.; Mock, J. J.; Justice, B. J.; Cummer, S. A.; Pendry, J. B.; Starr, A. F.; Smith, D. R. Metamaterial Electromagnetic Cloak at Microwave Frequencies. *Science* **2006**, *314*, 977–980.
- Cai, W.; Chettiar, U. K.; Kildishev, A. V.; Shalaev, V. M. Optical Cloaking with Metamaterials. *Nat. Photonics* **2008**, *1*, 224–227.
- Noginov, M. A.; Zhu, G.; Bahoura, M.; Adegoke, J.; Small, C. E.; Ritzo, B. A.; Drachev, V. P.; Shalaev, V. M. Enhancement of Surface Plasmons in an Ag Aggregate by Optical Gain in a Dielectric Medium. *Opt. Lett.* **2006**, *31*, 3022–3024.
- Gersten, J.; Nitzan, A. Spectroscopic Properties of Molecules Interacting with Small Dielectric Particles. *J. Chem. Phys.* **1981**, *75*, 1139–1152.
- Das, P. C.; Puri, A. Energy Flow and Fluorescence near a Small Metal Particle. *Phys. Rev. B* **2002**, *65*, 155416.
- Weitz, D. A.; Garoff, S.; Gersten, J. I.; Nitzan, A. The Enhancement of Raman Scattering, Resonance Raman Scattering and Fluorescence from Molecules Adsorbed on a Rough Silver Surface. *J. Chem. Phys.* **1983**, *78*, 5324–5338.
- Ritchie, R. H. Surface Plasmons in Solids. *Surf. Sci.* **1973**, *34*, 1–19.
- Moskovits, M. Surface-Enhanced Spectroscopy. *Rev. Mod. Phys.* **1985**, *57*, 783–826.

14. Quinten, M.; Leitner, A.; Krenn, J. R.; Aussenegg, F. R. Electromagnetic Energy Transport via Linear Chains of Silver Nanoparticles. *Opt. Lett.* **1998**, *23*, 1331–1333.
15. Averitt, R. D.; Westcott, S. L.; Halas, N. J. Linear Optical Properties of Gold Nanoshells. *J. Opt. Soc. Am. B* **1999**, *16*, 1824–1832.
16. Brongersma, M. L.; Hartman, J. W.; Atwater, H. A. Electromagnetic Energy Transfer and Switching in Nanoparticle Chain Arrays below the Diffraction Limit. *Phys. Rev. B* **2000**, *62*, R16356–R16359.
17. Mock, J. J.; Barbic, M.; Smith, D. R.; Schultz, D. A.; Schultz, S. Shape Effects in Plasmon Resonance of Individual Colloidal Silver Nanoparticles. *J. Chem. Phys.* **2002**, *116*, 6755–6759.
18. Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, 1995.
19. Su, K.-H.; Wei, Q.-H.; Zhang, X.; Mock, J. J.; Smith, D. R.; Schultz, S. Interparticle Coupling Effects on Plasmon Resonances of Nanogold Particles. *Nano Lett.* **2003**, *3*, 1087–1090.
20. Quinten, M. Optical Effects Associated with Aggregates of Cluster. *J. Cluster Sci.* **1999**, *10*, 319–358.
21. Sudarkin, A. N.; Demkovich, P. A. Excitation of Surface Electromagnetic Waves on the Boundary of a Metal with an Amplifying Medium. *Sov. Phys. Tech. Phys.* **1989**, *34*, 764–766.
22. Nezhad, M. P.; Tetz, K.; Fainman, Y. Gain Assisted Propagation of Surface Plasmon Polaritons on Planar Metallic Waveguides. *Opt. Express* **2004**, *12*, 4072–4079.
23. Avrutsky, I. Surface Plasmons at Nanoscale Relief Gratings between a Metal and a Dielectric Medium with Optical Gain. *Phys. Rev. B* **2004**, *70*, 155416.
24. Seidel, J.; Grafstrom, S.; Eng, L. Stimulated Emission of Surface Plasmons at the Interface between a Silver Film and an Optically Pumped Dye Solution. *Phys. Rev. Lett.* **2005**, *94*, 177401.
25. Bergman, D. J.; Stockman, M. I. Surface Plasmon Amplification by Stimulated Emission of Radiation: Quantum Generation of Coherent Surface Plasmons in Nanosystems. *Phys. Rev. Lett.* **2003**, *90*, 027402.
26. Stockman, M. Spasers Explained. *Nat. Photonics* **2008**, *2*, 327–329.
27. Zheludev, N.; Prosvirnin, S.; Papasimakis, N.; Fedotov, V. Lasing Spaser. *Nat. Photonics* **2008**, *2*, 351–354.
28. Noginov, M. A.; Zhu, G.; Belgrave, A. M.; Bakker, R.; Shalae, V. M.; Narimanov, E. E.; Stout, S.; Herz, E.; Suteewong, T.; Wiesner, U. Demonstration of a Spaser-Based Nanolaser. *Nature* **2009**, *460*, 1110–1113.
29. Förster, T. Intermolecular Energy Migration and Fluorescence. *Ann. Phys.* **1948**, *2*, 55–75.
30. Doussineau, T.; Trupp, S.; Mohr, G. J. Ratiometric pH-Nanosensors Based on Rhodamine-Doped Silica Nanoparticles Functionalized with a Naphthalimide Derivative. *J. Colloid Interface Sci.* **2009**, *339*, 266–270.
31. Fernández-López, C.; Mateo-Mateo, C.; Alvarez-Puebla, R.; Pérez-Juste, J.; Pastoriza-Santos, I.; Liz-Marzán, L. Highly Controlled Silica Coating of PEG-Capped Metal Nanoparticles and Preparation of SERS-Encoded Particles. *Langmuir* **2009**, *25*, 13894–13899.
32. Rodríguez-Fernández, J.; Pérez-Juste, J.; de Abajo, F. J. G.; Liz-Marzán, L. M. Seeded Growth of Submicron Au Colloids with Quadrupole Plasmon Resonance Modes. *Langmuir* **2006**, *22*, 7007–7010.
33. Tovmachenko, O. G.; Graf, C.; van den Heuvel, D. J.; van Blaaderen, A.; Gerritsen, H. C. Fluorescence Enhancement by Metal-Core/Silica-Shell Nanoparticles. *Adv. Mater.* **2006**, *18*, 91–95.
34. Draine, B. T. In *Light Scattering by Nonspherical Particles: Theory, Measurements, and Applications*; Mishchenko, M. I., Hovenier, J. W., Travis, L. D., Eds.; Academic Press: New York, 2000.
35. Dulkeith, E.; Morteani, A. C.; Niedereichholz, T.; Klar, T. A.; Feldmann, J.; Levi, S. A.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Moller, M.; Gittins, D. I. Fluorescence Quenching of Dye Molecules near Gold Nanoparticles: Radiative and Nonradiative Effects. *Phys. Rev. Lett.* **2002**, *89*, 203002.
36. Lawandy, N. M. Localized Surface Plasmon Singularities in Amplifying Media. *Appl. Phys. Lett.* **2004**, *85*, 5040–5042.
37. Bhowmick, S.; Saini, S.; Shenoy, V. B.; Bagchi, B. Resonance Energy Transfer from a Fluorescent Dye to a Metal Nanoparticle. *J. Chem. Phys.* **2006**, *125*, 181102/1-6.