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Plasmonic Focusing Reduces Ensemble Linewidth of Silver-Coated Gold Nanorods

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ABSTRACT

Silver coating gold nanorods reduces the ensemble plasmon line width by changing the relation connecting particle shape and plasmon resonance wavelength. This change, we term "plasmonic focusing", leads to less variation of resonance wavelengths for the same particle size distribution. We also find smaller single particle linewidth comparing resonances at the same wavelength but show that this does not contribute to the ensemble linewidth narrowing.

The ensemble linewidth of a suspension of plasmonic nanoparticles is a convolution of the linewidth of individual particles and the distribution of their resonance wavelength. A narrow ensemble plasmon line width is desirable for most plasmonic applications such as sensors,[1–3] the enhancement of nonlinear optical effects,[4–6] light guiding,[7,8] labeling,[9] or tissue targeting.[10,11] A small single particle plasmon linewidth implies a long plasmon lifetime, a large field enhancement, and a high sensing sensitivity. This intrinsic single particle plasmon linewidth is determined by the amount of damping and mainly due to interband and intraband excitation of electron−hole pairs, thus temperature, frequency, and material dependent.[12] The plasmon resonance wavelength is strongly dependent on the nanoparticle shape; a narrow ensemble linewidth indicates therefore a low polydispersity of the plasmonic particles. The main factor influencing the resonance wavelength of rod-shaped particles is the aspect ratio via a linear relationship we term the "plasmon-shape relation". Hence, three factors effectively determine the ensemble plasmon linewidth: (I) the single particle linewidth, (II) the width of the distribution in aspect ratios in the sample, and (III) the slope of the plasmon-shape relation connecting aspect ratio to resonance wavelength (Figure 1).

We find that coating gold nanorods with a thin shell of silver leads to a strong reduction of the ensemble linewidth. The quantitative examination of this effect leads to the surprising finding that it is caused by a change in slope of the plasmon-shape relation (factor III), an effect we term "plasmonic focusing". The silver coating leaves the shape and size of the original gold nanorods intact, excluding factor II from the discussion. The contribution of the single particle line width to the observed ensemble linewidth (factor I) is complex due to simultaneous shifts in the central resonance wavelength. However, we are able to show by single particle experiments together with theoretical modeling that the single particle linewidth contribution actually counteracts plasmonic focusing.

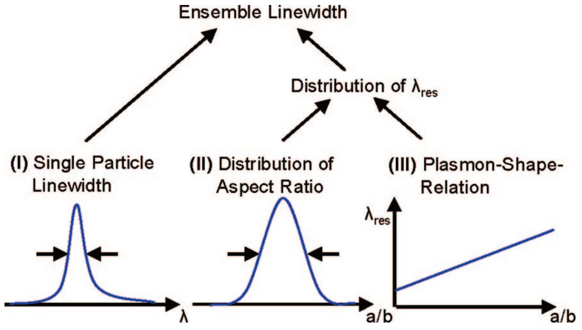

Figure 1. The three factors contributing to the ensemble plasmon linewidth: (I) the single particle linewidth, (II) the width of the distribution in aspect ratios (a/b) in the sample, and (III) the slope of the plasmon-shape relation connecting aspect ratio (a/b) to resonance wavelength (λ_{res}). A change in the slope of the plasmon-shape relation (III) is responsible for the ensemble linewidth narrowing of gold nanorods after silver coating.

To explain our term plasmonic focusing, we first note that during nanoparticle crystallization in solution, the shape and size polydispersity of the ensemble typically increases by statistical variations over time. An exception is the well-known (chemical) focusing regime during nanocrystal growth,[13–15] where a faster growth of small compared to

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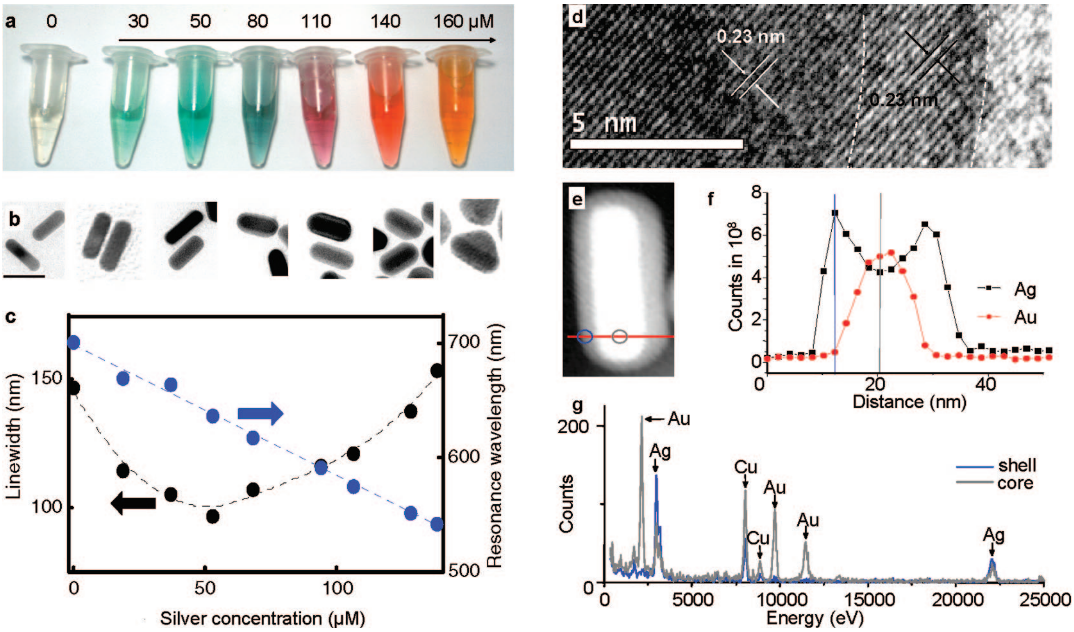

Figure 2. (a) True color photograph showing the color change of the pure gold nanorods (mean diameters 51 × 18 nm) (left sample) upon increasing silver concentration in the coating solution. The number above each vial indicates the concentration. (b) Representative TEM images corresponding to the samples shown above. They show the increasing thickness of the silver shell with increasing silver concentration becoming inhomogeneous at very high silver concentrations (scale bars for all images 50 nm). (c) Linewidth (black dots) and resonance wavelength (blue dots) as a function of silver concentration in the coating solution for a gold nanorod sample with a starting resonance wavelength of 700 nm and an initial line width of 148 nm. The shift in the resonance wavelength is approximately linearly dependent on the amount of silver present with a slope of -1.15 nm/μM (dashed blue line). The linewidth is the full width at half-maximum (fwhm) as determined directly from the spectra (Supporting Information, Figure S1). It shows a minimum at 53 μM, where it is reduced to 97 nm from the initial 148 nm (dashed black line is a guide to the eye). (d) High-resolution TEM image of a silver-coated gold nanorod. Dashed lines indicate the borders of the silver shell. Equal lattice spacing (0.23 nm) in the Au core and the Ag shell confirms epitaxial growth ([111] planes). (e) STEM image of the silver-coated gold nanorod with the position of the EDX linescan (red line). (f) Profile of the Au and Ag elemental distribution. (g) Two representative EDX spectra (at the positions indicated in (e) and (f)).

larger particles lets small particles “catch up”. This effectively narrows or focuses the nanoparticle size distribution. The plasmonic focusing we observe, where the plasmon resonance linewidth of an ensemble of gold nanorods is smaller after silver coating than before, leaves the gold nanoparticles shape undisturbed but rather changes the way their shape polydispersity translates into spectral polydispersity. A shallower slope of the plasmon-shape relation narrows or focuses the distribution of plasmon resonances. In the ideal case of a completely flat plasmon-shape relation, all particles would have the same resonance wavelength regardless of their aspect ratio leading to an ensemble linewidth only limited by the intrinsic single particle linewidth. Another way of looking at plasmonic focusing is observing the spectral shift induced by the silver coating. Silver coating generally leads to a blueshift, but the shift is stronger for particles with resonances further in the red.

Note the nontrivial choice of units in the discussion of linewidth changes accompanied with a resonance shift: a linewidth narrowing in energy or frequency units may correspond to a linewidth narrowing or broadening in wavelength units, depending on the magnitude of the resonance shift. Length or wavelength units have to be chosen here because of the almost linear relationship between aspect ratio and resonance wavelength.[16,17] Other geometric factors besides aspect ratio, namely, end-cap geometry and particle volume, have a weak influence on the plasmon resonance compared to the aspect ratio.[18,19] An ensemble linewidth in length units therefore relates to a certain polydispersity in aspect ratio regardless of the mean resonance wavelength. For other discussions, linewidth in energy units may be more appropriate, e.g., the single particles energy linewidth corresponds to the plasmon decay time.

We produce silver-coated gold nanorods according to literature[20] by adding preformed gold nanorods[21] to a coating solution containing silver ions (Supporting Information). Increasing the silver concentration in the coating solution leads to a strong color shift (from green to orange-yellow, Figure 2a). The different electron density of silver and gold makes it possible to visualize clearly the silver shell around the original gold nanorod in transmission electron microscopy (TEM). The images confirm the expected increase of the silver shell thickness with increasing concentration of silver in the coating solution. When the silver concentration gets too high, the shell grows inhomogeneously (Figure 2b). High-resolution TEM and spatially resolved elemental analysis by nanospot energy dispersive X-ray spectroscopy (Figure 1d−g and Supporting Information, Methods Section) confirm the monocrystallinity of the particles, the epitaxial growths of the silver shell on the gold particles.

Extinction spectra of the solutions reveal a blueshift of the plasmon resonance wavelength of up to 150 nm (Figure 2c and Supporting Information, Figure S1), which is approximately linearly dependent on the amount of silver

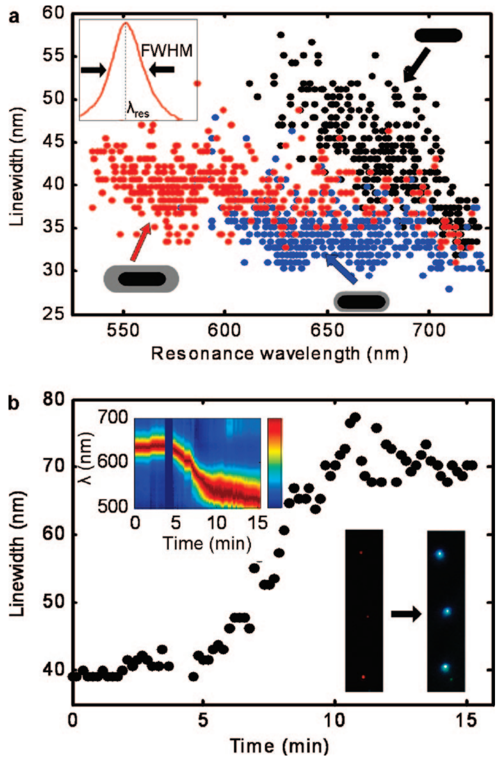

Figure 3. (a) Linewidth of gold nanorods (without coating (black dots), with a thin (blue dots) and thick (red dots) silver shell) plotted against their resonance wavelength, both extracted directly from scattering spectra (inset). On average, the linewidth (fwhm) of particles with silver coating is smaller than the linewidth of pure gold nanorods with similar resonance wavelength. The thicker silver shell shows a higher linewidth than the thin shell due to an anisotropic shell thickness. (b) Observation of the linewidth change over time of a single gold nanorod exposed to the silver-coating solution. The inset on the upper left shows the full spectra (color coded) over time and the inset on the lower right a true color photograph of the same particles in the dark-field microscope before and after coating.

present (slope about −1.15 nm/μM). The extinction spectra also show the strong narrowing of the plasmon resonance in the particle ensemble spectra after silver coating when compared to the linewidth of the original gold nanoparticles—at least for thin silver coating. This narrowing has to the best of our knowledge not been reported before and is only observable if the silver shell is very homogeneous.[20,22–27] As is evident from Figure 2b, a slightly thicker silver layer typically leads to more inhomogeneous coating resulting in a broadening of the ensemble linewidth compared to the optimal silver thickness.

Before discussing the ensemble linewidth narrowing by plasmonic focusing in detail, we will first examine the single particle linewidth for coated and uncoated nanoparticles by observing the scattered light of individual nanoparticles in a dark-field microscope.[12,22,28] Our setup is automated to allow the spectral investigation of several hundred nanoparticles with reasonable effort.[29] For each particle spectrum, we extract the mean resonance position (λ_{res}) and the full linewidth at half of the maximum intensity Γ_{SP} (cf. Figure 3a inset). Because the excitation of d-band electrons into the conduction band requires a threshold energy, the linewidth increases for higher frequencies or smaller wavelengths. Hence, a plot of single particle linewidth Γ_{SP} as a function of the resonance wavelength λ_{res} shows an increase of linewidth at smaller wavelengths (Figure 3 and Supporting Information, Figure S6). Most importantly, we observe a decrease of the single particle linewidth Γ_{SP} after silver coating compared to uncoated particles *at the same resonance wavelength* λ_{res}. This decrease is largest for thin coatings and less pronounced for a thicker silver shell. The silver shell reduces the plasmon damping due to the higher energy required to excite d-band electrons into the conduction band in silver compared to gold. The interface between the gold core and the silver shell causes apparently no additional damping. A smaller single particle linewidth means lower plasmon damping, thus a longer plasmon lifetime (cf. Supporting Information, Figure S2) and a higher field enhancement, which is beneficial for many plasmonic applications. The quality factor Q (relevant for the field enhancement around plasmonic particles) increases for silver-coated rods compared to gold rods at the same resonance energy (Supporting Information, Figure S3). For example, at 670 nm, we find silver-coated gold rods with quality factors above 20, whereas uncoated rods show quality factors below 15. The enhancement of Raman signals[5] is believed to depend on Q^4, so the silver-coated gold rods should show an improvement of more than $(20/15)^4 \approx 3$. The increase of the single particle linewidth for a thick silver coating (compared to a thin coating) is probably due to the variation in the shell thickness around each particle—as already observed in TEM (Figure 2b). If the silver layer becomes too thick, the particles start to lose their rodlike shape. Affirming the hypothesis of decreasing rodlike shape, we observe a decrease in the optical polarization anisotropy for rods with thicker silver coating (Supporting Information, Figure S4).

The smaller linewidth of silver-coated gold rods compared to uncoated gold rods *at the same resonance wavelength* is, however, not responsible for the observed linewidth narrowing of the *ensemble* linewidth. The reason is the simultaneous shift in resonance wavelength toward regions with intrinsically higher plasmon damping. Depending on the initial and final wavelength, this shift in resonance wavelength often results in a broadening of the linewidth of a given particle after coating with silver. We observe such plasmon linewidth broadening of an individual particle by continuously monitoring individual particles exposed to a coating solution (Figure 3b and Supporting Information, Methods Section).

If the single particle linewidth of particles becomes broader after silver coating, why do we observe a narrowing of the ensemble linewidth? The answer is a change in the plasmon-shape relation, which converts the distribution of particle aspect ratios into a distribution of plasmon resonances. In chemical focusing during nanocrystal growth, the growth of small particles is favored. Here, the silver coating shifts the plasmon resonances stronger for rods with higher aspect ratio than for particles with lower aspect ratio. Therefore, the same

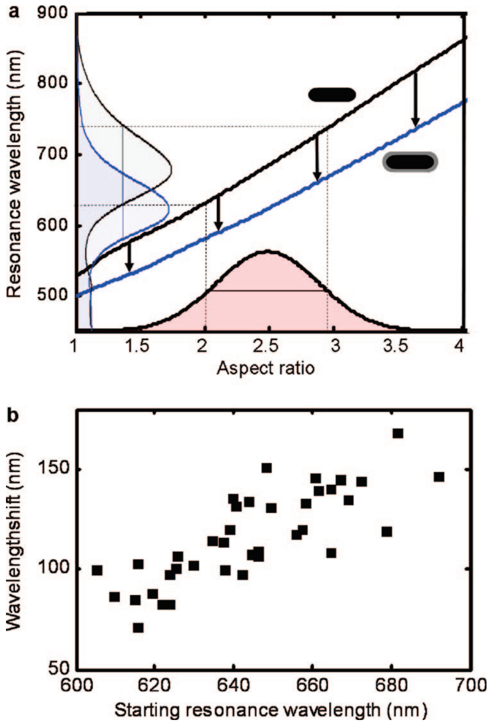

Figure 4. (a) The plasmon-shape relation shows how the resonance wavelength depends on aspect ratio. Values derived theoretically within the quasi-static approximation are shown for gold rods in water (black line, $n = 1.33$) and with a 2.3 nm silver coating (blue line). The plasmon-shape relation converts an ensemble of particles with a distribution of aspect ratios (indicated by pink shading) into a distribution of resonance wavelengths (indicated by the gray shaded spectrum). The plasmon-shape relations are almost linear, i.e., a distribution of aspect ratios with a given width (polydispersity) gives a certain linewidth regardless of the mean aspect ratio. The smaller slope of the plasmon-shape relation for the silver-coated rods leads to a smaller spectral linewidth (blue shaded spectrum). An alternative way to look at the effect of coating is to observe the vertical differences between the two plasmon-shape relations (indicated by black arrows). Rods with higher aspect ratio shift more on silver coating than those with a smaller aspect ratio (b) Experimental data for the wavelength shifts of gold nanorods upon coating with silver as a function of the starting resonance wavelength. Each data point is extracted from two single particle measurements of the same particle before and after coating. Higher starting resonance wavelengths, i.e., rods with higher aspect ratio, result in larger wavelength shifts.

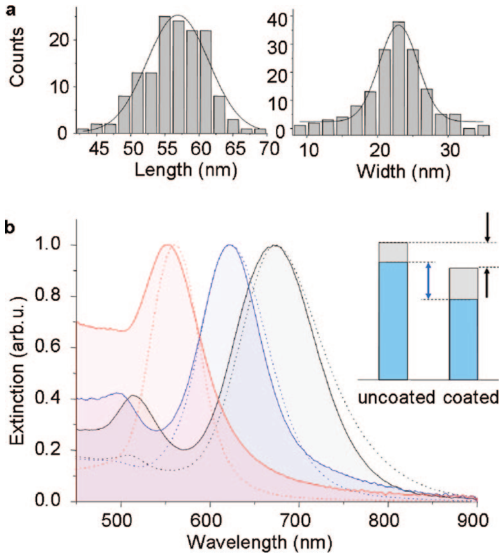

Figure 5. (a) Length and width distribution of a sample of uncoated gold nanorods as determined from TEM images of 145 particles. The length and width show a mean of 56.4 ± 4.4 and 22.8 ± 3.4 nm, respectively. (b) Ensemble extinction spectra of this gold nanoparticle sample (black) with a thin (2.3 nm) silver coating (blue) and a thick coating (6.9 nm, red): solid lines measured, dashed lines calculated. Only one free parameter enters all three calculations: the eccentricity e used to calculate the geometrical "L factor",[18] here $e = 0.95$. All other parameters are determined by TEM. The calculated spectra show good agreement to the measurement in both resonance position and linewidth. The inset illustrates the (calculated) linewidth for the uncoated and thinly coated nanorods, in black/gray including the single particle contribution and in blue without this contribution (i.e., pure plasmonic focusing).

particle distribution leads to a narrower distribution of plasmon resonances after coating due to a different slope in the plasmon-shape relation (Figure 4a). This purely electrodynamic effect that we call plasmonic focusing is responsible for the observed narrowing of the ensemble linewidth. The shallower slope of the plasmon-shape relation for silver-coated particles is caused by the strong wavelength dependency of the dielectric function of silver due to the plasma of the quasi free conduction band electrons. There are two equivalent ways to look at plasmonic focusing: by noting the change in the slope in the plasmon-shape relation or by considering the plasmon shifts after coating. The latter lets us verify the theoretical model by spectrally investigating the same particles before and after coating without knowing the precise aspect ratio. We expect to find that particles with longer resonance wavelengths (i.e., larger aspect ratio) show a larger plasmon shift than those with a shorter starting wavelength. Indeed, we observe this trend (Figure 4b).

The plasmon-shape relation in Figure 4a is derived from an electrodynamic model based on the quasi-static approximation[20] (Supporting Information, Methods Section). We test whether this model is able to predict the measured ensemble spectra from a known particle shape distribution, which we obtain by measuring the width and length of about 150 particles per sample on TEM images (Figure 5a). The simulation using our electrodynamic model reproduces the observed spectrum well, both for the uncoated and for the coated particles (Figure 5b). The shell thicknesses used here are inferred from TEM analysis, there are therefore no free parameters entering the calculation. Hence, we are confident that this simple method predicts ensemble plasmon wavelength and linewidth accurately. The model lets us theoretically analyze how strong the plasmonic focusing effect would be if the single particle linewidth remained constant after coating. Since the single particle linewidth increases after coating, it effectively reduces the amount of linewidth narrowing observable in the ensemble spectra. The convolution of single particle linewidth with the distribution of resonances in the ensemble further weakens the effect of any reduction of either of the two parameters. We show the values for the ensemble linewidth with and without the single particle contribution in the inset to Figure 5b. The plasmonic focusing alone would reduce the linewidth from

97 to 66 nm; the single particle line width increases from 28 to 29 nm. Their convolution then changes from 113 to 92 nm, which compares well to the measured change from 112 to 88 nm. Other samples show similarly good agreement of theory and experiment (Supporting Information, Figure S5).

Our analysis of the plasmon linewidth of silver-coated gold nanorods shows two surprising and important results: ensemble linewidth narrowing by plasmonic focusing and single particle linewidth narrowing, comparing particles *with the same resonance wavelength*. Even though silver-coated nanoparticles have been prepared and studied before, the linewidth narrowing of both the ensemble and of single particles has not been reported—probably because it is only present for very homogeneous silver shells. Only the spectroscopic investigation of several hundred single particles using an advanced single particle spectroscopy approach made it possible to obtain enough statistics to compare particles at the same resonance wavelength. Each individual particle shifts in resonance wavelength after silver coating, but observing many different particles allows comparing pairs with the same resonance wavelength. Since the damping (and thus the single particle line width) changes with resonance wavelength, only this direct comparison at the same wavelength makes sense.

In combination with extensive particle size analysis by TEM, our electrodynamic model allows entangling the contributions of single particle linewidth and plasmonic focusing for the observed ensemble linewidth changes. Plasmonic focusing alone would reduce the ensemble linewidth by about 30%; the convolution with single particle linewidth reduces the effect to about 20%. Plasmonic focusing is a new feature of bimetallic core−shell structures, interesting from a fundamental point of view. A sample preparation strategy with plasmonic focusing provides a simple method to obtain high-quality plasmonic particles with tunable resonance energy over the entire visible spectrum. The silver-coated gold nanoparticles we produce are among the best plasmonic structures known with up to 50% longer plasmon lifetime than gold nanorods at the same resonance energy, which will make them ideal candidates for the enhancement of nonlinear effects, sensing, and light-guiding applications.

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Supporting Information Available: A method section describing the synthesis and characterization of the initial gold nanorods and the silver coating, details of the continuous investigation of the coating process on the single particle level and of the electrodynamic model to calculate the ensemble extinction spectra, and supplemental figures showing the normalized extinction spectra of the silver-coated particles (Figure S1), the linewidth of single particle scattering spectra vs their resonance energy (Figure S2), the quality factor of pure and silver-coated gold nanorods (Figure S3), the polarization anisotropy of the particles (Figure S4), additional examples of measured and calculated ensemble spectra (Figure S5), and a second sample showing the decrease of the single particle linewidth for silver-coated particles (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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