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Correlated Optical Spectroscopy and Transmission Electron Microscopy of Individual Hollow Nanoparticles and their Dimers

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Abstract

The optical spectra of individual Ag-Au alloy hollow particles were correlated with the particles' structures obtained by transmission electron microscopy (TEM). The TEM provided direct experimental access to the dimension of the cavity, thickness of the metal shell, and the interparticle distance of hollow particle dimers with high spatial resolution. The analysis of correlated spectral and structural information enabled the quantification of the influence of the core-shell structure on the resonance energy, plasmon lifetime, and plasmon coupling efficiency. Electron beam exposure during TEM inspection was observed to affect plasmon wavelength and lifetime, making optical inspection prior to structural characterization mandatory.

The vivid and lasting colors of noble metal nanoparticles have long intrigued humans, and even today more than 100 years after the pioneering work of Zsigmondy on gold colloids,¹ noble metal nanoparticles remain the subject of intense research. They are considered to be key components of future applications in photonics,³ electronics,⁴ and biotechnology^{5,6}. The main interest in noble metal nanoparticles is stimulated by their interactions with light. Incident light fields induce collective oscillations of the conduction band electron in the particles.^{7,8} These oscillations are referred to as plasmons. If the incident light is in resonance with the particle plasmon, small incident fields can lead to strong electron oscillations, resulting in large optical cross-sections and strong fields in the vicinity of the particles. Due to the strong *E*-field enhancement in the vicinity of noble metal nanoparticles, these particles have long been used as substrates in field enhanced spectroscopy such as surface enhanced Raman spectroscopy (SERS).^{9–12}

In analogy to molecules that have properties differing from those of the atoms they consist of, two and three dimensional assemblies of nanoparticles can create additional functionalities beyond those of the individual nanoparticles.¹³ The near-field coupling between individual nanoparticles leads to a strong field enhancement in the center of the dimer junctions, localizing incident light fields in a small volume.^{14,15} Also, plasmon polaritons can propagate along a chain of coupled nanoparticles enabling the design of waveguides with lateral dimensions significantly below the diffraction limit.^{16,17} Another important area of applications for discrete assemblies of coupled nanoparticles lies in the field of biosensors. Polymer tethered pairs of nanoparticles are emerging as versatile and sensitive sensors.¹⁸ Individual pairs of DNA and RNA linked nanoparticles have successfully been used as plasmon rulers for measuring distances and distance changes in single biopolymers.^{19–21}

Given the wealth of potential applications for noble metal nanoparticles with defined plasmon resonances, there have been considerable efforts to develop wet-chemical synthesis procedures

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to control the shape, size, and composition of nanoparticles.^{22–24} One of the most intriguing structures is a dielectric core that is surrounded by a thin gold or silver shell. These core-shell particles are usually referred to as nanoshells if the core consists of a solid dielectric such as silica. They are referred to as “hollow shells” or simply “hollow particles” if the particles consist only of a shell around a cavity that is filled with solvent. Aden and Kerker²⁵ were the first to develop a theoretical treatment of metal nanoshells based on Mie theory²⁶, and Halas and coworkers^{22,27–29} pioneered their experimental realization and exploration. One important characteristic of metallic nanoshells and hollow nanostructures is that their plasmon resonance can be tuned from the green all the way into the infrared through variation of the ratio of inner and outer diameter.^{27,30–32} Since the shells in these particles contain inner and outer surfaces that are only divided by a few nanometers, the plasmons on both surfaces can couple resulting in strong field intensities in the surrounding of the particles.²⁹ Consequently, metallic nanoshells have attracted much interest as efficient SERS substrate that can be tuned to a specific wavelength.^{33–35}

The possibility to tune the optical properties of individual metal hollow particles has prompted our interest in these particles as building blocks for nanostructured devices based on plasmon coupling. Ag-Au hollow particles are particularly interesting as building blocks for plasmonic devices as they could facilitate discrete nanoparticle assemblies with plasmon resonances in the biological water window between 700–1100 nm for applications as biomedical sensors. The design of functional plasmonic devices based on individual nanostructures requires a precise knowledge of the characteristics of the individual components as well as their interactions in assemblies. To overcome the ensemble averaging over different particle sizes and shapes in bulk studies, these properties are best studied at the single particle level.^{36–41} Ideally, optical single particle measurements are thereby combined with a high resolution structural characterization of the individual particles. In the case of gold nanoshells and metallic hollow nanostructures single particle optical spectroscopy combined with Atomic Force Microscopy (AFM) or Scanning Electron Microscopy (SEM) has contributed significantly to our current understanding of the structure-spectrum relationships.^{36–39} Since the spatial resolutions of the SEM and AFM impede a precise measurement of interparticle distances in close-by particles and since they cannot precisely quantify the shell thickness, these studies were in some cases augmented with simulations to derive inaccessible structural parameters.⁴² We take here an alternative approach and correlate single particle spectroscopy with transmission electron microscopy. This enables us to experimentally determine all relevant structural parameters including the shell thickness and interparticle distance for dimers. We apply this approach to correlate the homogenous linewidth Γ_{hom} of individual hollow particles and the plasmon resonance energy E_{res} of Ag-Au alloy hollow particles and their dimers with structural parameters such as the particle diameter, shell thickness and interparticle distance.

Experimental Procedures

Synthesis of hollow Ag-Au alloy particles

We synthesized Ag-Au hollow particles with two different average sizes via a galvanic replacement approach as described by Xia and coworkers³⁰ using commercial 20 ± 2 nm and 40 ± 4 nm silver seeds. In a typical reaction, 10 mL commercial colloids were diluted with 20 mL DDI water (double distilled, 18.2 M Ω) and refluxed for 10 min. Then 1 mL 0.1 mM HAuCl₄ aqueous solution was added to the reaction by rapid injection. The reaction mixture was refluxed for another 30 min when its color became stable. Vigorous magnetic stirring was maintained during the entire process. Finally, the hollow particles were washed twice by centrifugation. In the case of 20 nm seeds we obtained Ag-Au alloy hollow particles with an average outer diameter $\bar{d}_{\text{out}} = 53.0 \pm 4.0$ nm and average shell thickness of 8.6 ± 2.0 nm. 40 nm Ag seeds led to a diameter of $\bar{d}_{\text{out}} = 96.9 \pm 8.1$ nm and a shell thickness of 13.2 ± 2.3 nm.

We will refer to particles of these two batches in the following as HP1 ($\bar{d}_{out} = 53.0 \pm 4.0$ nm) and HP2 ($\bar{d}_{out} = 96.9 \pm 8.1$ nm). We ascribe the observed increase in particle diameter in the course of the replacement reaction to the nanoscale Kirkendall effect.⁴³ The surface reaction between the silver and the gold salt on the particle surface leads to the diffusion of the silver from the core into the shell resulting in an overall increase in particle diameter while hollowing out the particle creating a void.

After synthesis, the particles were stabilized by assembly of a monolayer of short carboxy-terminated polyethylene glycols (O-(2-Carboxyethyl)-O'-(2-mercaptoethyl)-heptaethylene glycol). For UV-Vis and TEM characterization of the Ag-Au hollow particles please refer to Figure S1 in the Supporting Information.

Correlated darkfield spectroscopy and transmission electron microscopy

Our experimental approach is a modification of the procedure developed by Mock *et al.*⁴⁴ The samples were prepared by spin-coating a dilute solution of Ag-Au hollow nanoparticles in 0.5% gelatin onto formvar coated copper finder grids (Gilder TEM binary system finder grid) at 3000 rpm. The gelatin facilitated an easy spin-coating of the particles and served as matrix to immobilize the particles on the substrate. We determined the thickness of the polymer film after spincoating with ellipsometry to be ~ 8 nm. After spincoating the sample substrates were dried overnight at room temperature. Recent work by Novo *et al.*⁴⁵ has highlighted the influence of the micronenvironment on the optical properties of spincoated nanoparticles. We minimized variations in the refractive index in the surrounding of the particles through immersion of the spincoated samples in index matching glycerin ($n_r = 1.47$). The samples were then sandwiched between two glass coverslips, and imaged in an optical microscope. The samples were illuminated with unpolarized white light from a 100W Tungsten lamp through an oil darkfield condenser (numerical aperture, NA = 1.2–1.4). The light scattered off individual, spatially isolated light emitters was collected with a 40x objective (NA = 0.65) and injected into a 150 mm focal length imaging spectrometer (Acton Research, InSpectrum 150) with a back-illuminated CCD detector (Hamamatsu INS-122B) for spectral analysis. Additional information about the polarization state of the scattered light was obtained by inserting an analyzer into the light path in front of the detector and recording scattering spectra as a function of the analyzer angle. After the optical measurements, all glycerin was removed from the samples by immersion in methanol for 10–20 seconds. The samples were dried and transferred for inspection into the TEM (JEOL 2010) operated at an acceleration voltage of 80 kV.

Results and Discussion

Individual Ag-Au alloy hollow particles of both particle batches HP1 ($\bar{d}_{out} = 53.0 \pm 4.0$ nm) and HP2 ($\bar{d}_{out} = 96.9 \pm 8.1$ nm) were easily detected as bright spots in the focal plane of the dark field microscope (see Figure 1a)) and amenable to spectral characterization (see Figure 1b)). The plasmon resonance energy E_{res} of an individual particle was obtained by fitting its spectrum with a single Lorentzian. The correlation of the spectrum of an individual particle with its structure was achieved by using the spatial distribution of the Ag-Au hollow particles on the TEM grid (Figure 1c)) as internal marker to correlate the electron microscope micrograph with the image from the optical microscope (Figure 1a)). Patterns of individual particles observed in the optical microscope were found again in the TEM at low magnification (2,000x). Structural details of the assigned particles, such as the geometry, shape, inner and outer particle diameter, were then determined at high magnification (100,000x).

The TEM image in Figure 1d) belongs to the particle No. 5 in Figure 1c) whose spectrum is shown in Figure 1b). In the TEM image the metal shell is clearly visible due to its higher contrast compared to the central cavity region. This enables us to determine the ratio of inner

and outer diameter which is a characteristic parameter for the resonance energy in core-shell particles.⁴⁶ Most of the investigated particles were not perfectly symmetric and the ratio of inner and outer diameter along different axes could vary by up to ~10%. To account for these intrinsic asymmetries we averaged the ratio of inner and outer diameter along two

perpendicular axes and calculated R values defined as $R = \frac{1}{2} \left[\frac{d_{in}^1}{d_{out}^1} + \frac{d_{in}^2}{d_{out}^2} \right]$ (see Figure 1d)). Having in hand a method to correlate the R value of an individual particle with its spectrum we set out to explore the quantitative relationships between the particle structure and its optical properties.

E_{res} vs. R relationship for hollow particles with different sizes

Since the plasmon resonance of an individual Ag-Au alloy particle depends both on its structure and composition,⁴⁷ it was first necessary to determine the variability in elemental composition for the particles. We measured the elemental composition of ten randomly selected particles for both hollow particle sizes by energy dispersive X-ray spectroscopy (EDAX). In case of HP1 the average composition was 65% Ag and 35% Au (atomic ratio) whereas for the bigger HP2 the average composition was 75% Ag and 25% Au. The absolute error in elemental composition in both cases was 5%. EDAX linescans for individual particles (see Figure S2, Supporting Information) revealed that the variations of the elemental composition within the particles were also on the order of 5%. These measurements confirm a uniform Ag, Au distribution and homogenous extent of alloying within the particles. Based on previous studies of the optical properties of solid Ag-Au particles as function of alloy composition,⁴⁸ we estimate that composition variations on the order of 5% can lead to variations in the resonance energy of $|\Delta E_{res}| \leq 25$ meV.

In Figure 2 we show E_{res} as function of R for HP1 and HP2 particles. The experimental values are broadly distributed around a general trend: E_{res} decreases as function of R . The broad spread of the experimental data arises from particle-to-particle variations in the elemental composition and particle structure. A single structural parameter, in our case R , cannot capture all the structural details that govern the plasmon resonance of a complex nanostructure such as a hollow nanoparticle. Due to the intrinsic anisotropy of the individual particles R is only an approximation of all the relevant structural parameters. The accuracy of this approximation is expected to decrease with growing particle size since the structural heterogeneity increases. Indeed we find that the E_{res} values are more broadly spread for the larger HP2 particles.

Given the spread of the experimental data we chose a linear fit as the simplest possible functional relationship to quantify the global trend in the E_{res} vs. R relationships for HP1 and HP2. The linear fits defined by the functional relationships $E_{res}(\text{HP1}) = 2.52 \text{ eV} - 0.93 \text{ eV} * R$ ($R = [0.53, 0.77]$, correlation coefficient $\rho(\text{HP1}) = 0.81$) and $E_{res}(\text{HP2}) = 2.77 \text{ eV} - 1.31 \text{ eV} * R$ ($R = [0.59, 0.83]$, $\rho(\text{HP2}) = 0.70$) are included in Figure 2 as dashed lines. The choice of a linear fit was further motivated by simulations of the E_{res} vs. R relationship in Ag-Au alloy hollow particles included in Figure 2 as green triangles. These simulations were performed for hollow particles with a fixed outer diameter of 100 nm using the discrete dipole approximation (DDA)² method. We took the dielectric function shown in Moskovits *et al.*⁴⁸ for solid Ag-Au alloy nanoparticles with an Au mole fraction of 0.2, which is close to the elemental composition of our HP2 particles, and assumed glycerin with a refractive index of $n_r = 1.47$ as core and surrounding medium. The resulting peak resonance energy versus R relationship is well described by linear fit of the form: $E_{res}(\text{HP2}) = 2.11 \text{ eV} - 0.38 \text{ eV} * R$ ($R = [0.53, 0.80]$, $\rho = 0.99$).

The simulations and the experimental data agree qualitatively; however the experimental E_{res} vs. R relationship shows a stronger dependency on R than predicted by the simulation. The slopes of the $E_{res}(R)$ fits are significantly steeper in the experimental data than in the simulations. Especially for R values < 0.66 the agreement between simulated and measured

E_{res} values is only poor. Quantitatively correct simulations of the optical properties of Ag-Au alloy hollow particles are challenging. They require precise knowledge of the dielectric function of the alloy⁴⁷ as well as a computational approach capable of an accurate modeling of the electrodynamic response of hollow particles that are embedded in a polymer matrix and deposited on a surface. Our approach sidesteps these problems since it enables us to directly measure the relevant structural and spectral properties experimentally. The experimental $E_{res}(R)$ relationships shown in Figure 2 can serve as benchmark to further improve the accuracy of future numerical simulations of Ag-Au alloy hollow particles.

Plasmon lifetimes in individual hollow particles

The plasmon linewidth is another important factor that influences the usefulness of a nanoparticle in applications. For particle plasmon based sensors that rely on shifts in E_{res} as the observable, sharp resonances increase the resolution.⁵⁰ As discussed elsewhere,⁵¹ the linewidth of the resonance has general implications for all non-linear applications of particle plasmons such as SERS. Plasmon line widths of several particle shapes such as solid spheres,⁵¹ rods,^{51–53} gold nanoshells,³⁶ core-shell Ag-Au nanorods,⁵⁴ and Ag-Au nanoboxes, nanocages^{37,52,55} and nanoprism⁴⁰ have been investigated at the single particle level. These studies were motivated by the fact that single particle spectroscopy can overcome the heterogeneous lifetime broadening in bulk samples, so that the width of the measured plasmon corresponds to its homogenous linewidth that can be directly converted into the plasmon lifetime.⁵¹ For particles that are not ideally symmetric spheres the particles' anisotropy needs to be considered. Asymmetric particle structures give rise to different plasmon modes along different particle axes. Under unpolarized white light illumination, all of these modes will be excited simultaneously leading to an anisotropic broadening of the plasmon resonance. The plasmon modes along different particle axes can be resolved by inserting an analyzer into the beam path in front of the spectrometer and recording the plasmon spectra as function of the polarization state. We used this polarization sensitive detection scheme to eliminate all hollow particles that showed a strong anisotropic plasmon broadening. We included in our analysis only those particles whose plasmon resonance energies differ on any two axes by no more than 40 meV. From particles that fulfilled this criterion we determined an approximate homogenous linewidth Γ_{hom} by averaging the full width at half maxima (FWHM) obtained from Lorentzian fits to spectra recorded at four different analyzer angles (0°, 45°, 90°, 135°). Following this procedure we obtained an approximated homogenous linewidth for spherical hollow particles of $\Gamma_{hom} = 307 \pm 49$ meV for HP1 and 283 ± 25 meV for HP2.⁵⁶

Next, we investigated the dependence of Γ_{hom} on E_{res} . As shown in Figure 3a, Γ_{hom} increases continuously as function of E_{res} . We have included a linear fit $\Gamma_{hom} = -0.27 \text{ eV} + 0.31 * E_{res}$ ($E_{res} = [1.70, 2.04]$, $\rho(\Gamma_{hom}) = 0.648$) of the combined data sets as a continuous line in Figure 3a. A similar increase in linewidth as function of resonance energy was observed before in solid Ag-Au alloy particles and Au(core)-Ag(shell) particles where this behavior was ascribed to the frequency dependence of the dielectric constants.⁴¹ With the onset of the Au 5d → 6sp interband transitions at ~1.8 eV⁷ plasmon decay by excitation of a d band electron into the conduction band becomes possible.⁵¹ Consequently, Γ_{hom} increases with E_{res} due to a more efficient interband damping. Other effects that influence the linewidth in Ag-Au alloy hollow particles of different sizes are phase retardation,^{7,41,52,57} and – due to the thinness of the shells in our particles – surface scattering^{7,57,58} of the electrons. The fact that the smaller HP1 particles have on average broader linewidths than the larger HP2 particles indicates that the contribution of radiation damping due to electromagnetic retardation – which is expected to increase with particle size^{41,52} – is small compared to that of the frequency dependent interband damping.

The effect of the surface scattering of the conduction electrons is less obvious. Our approach to correlate the spectra of individual particles with the ratio of inner and outer diameter, R , enables us to probe the dependence of Γ_{hom} on the shell thickness. To that end we define a normalized shell thickness T as the ratio of the shell thickness divided by total particle radius. T is readily calculated as $T = 1 - R$. In Figure 3b we plot Γ_{hom} as function of T for both investigated particle sizes HP1 and HP2. Γ_{hom} overall increases with increasing T revealing that particles with thinner shells have on average sharper plasmon resonances. This finding suggests that in the case of our Ag-Au alloy hollow particles the contribution from surface scattering to the lifetime broadening is smaller than that of interband damping. In fact, our studies suggest that for hollow particles in which interband transitions are accessible ($E_{\text{res}} > 1.8$ eV), Γ_{hom} can be minimized by increasing R . We expect that for very thin shells surface scattering will become the dominant damping factor, however, for the particles under investigation here with diameters between 50 – 100 nm and $R \leq 0.8$ this is not the case.

Effect of electron beam (e-beam) on plasmon resonance energy E_{res} and homogenous linewidth Γ_{hom}

In a second set of experiments we reversed the order of our correlation process: we characterized the HP2 hollow particles in the TEM before optical inspection in the microscope. It was immediately noticeable that the particles were dimmer after exposure to an 80 keV e-beam (~ 200 pA/cm²). Next to this change in scattering intensity, we also observed changes in the plasmon resonance wavelength and linewidth. The two spectra in Figure 4a) belong to the same HP2 hollow particle before and after e-beam exposure. After inspection in the TEM the spectrum was red-shifted and the plasmon linewidth Γ_{hom} was significantly broadened. The particle shown in Figure 4a is not a special case, additional spectra of particles before and after e-beam exposure are shown in Figure S3 (see Supporting Information). As consequence of these initial observations we started a systematical investigation to quantify the average effect of the e-beam. In Figure 4b) distributions of E_{res} for HP2 particles measured before and after e-beam exposure are shown. The distributions of the particles measured after e-beam exposure is red-shifted by ~ 200 meV. The effect on the homogenous linewidth is even more pronounced; after e-beam exposure the average linewidth Γ_{hom} has increased to 619 ± 163 meV, compared to $\Gamma_{\text{hom}} = 283 \pm 25$ before e-beam exposure.

What is the reason for this drastic effect of the e-beam on the optical properties of the hollow particles? It is known that Au nanoparticles can undergo structural changes when they are exposed to an intense e-beam irradiation.^{59,60} However, we could not find experimental proof that e-beam induced structural changes are the reason for the observed spectral shifts. Based on the $E_{\text{res}}(R)$ relationship for HP2 hollow particles in Figure 2, we approximate that a change in shell thickness of > 2.5 nm is required to red-shift E_{res} of an HP2 particle by 200 meV. Changes of this magnitude can clearly be resolved with the TEM. However, we did not detect obvious changes in the particle geometry or shell thickness of hollow particles when we moved the e-beam to a new area of the TEM grid and then focused on an individual hollow particle for up to 10 minutes. Based on these experiments we discard the hypothesis of a structural reorganization as reason for the spectral shift. Instead, we propose that the spectral change is due to an e-beam stimulated reaction⁶¹ of the Ag-Au alloy with the surrounding organic polymer. It is well known that an oxidation of silver particles leads to a spectral red-shift and a broadening of the plasmon resonance.⁶² We believe that the observed perturbation is not specific for Ag-Au alloy hollow particles imaged by TEM. In the case of nanofabricated gold structures changes of optical properties upon inspection by SEM have also been noted.³⁹ These earlier observations and our findings here have implications for future correlated electron microscopy and single particle spectroscopy studies in general. In order to avoid any impairment of the optical properties of the nanostructure, the optical characterization should always be carried out prior to the structural characterization.

Plasmon coupling between individual Ag-Au alloy hollow particles

The spin-coated hollow particle samples also contained randomly formed dimers. These dimers offered the opportunity to study plasmon coupling between individual Ag-Au alloy hollow particles with different interparticle separations. With the TEM we could resolve interparticle separations of approximately 1 nm; we will refer to interparticle separations below this spatial resolution as “touching” in the following. Figure 5 contains the spectra of three different hollow particle dimers with different interparticle distances. The interparticle separation increases from < 1 nm (touching) in Figure 5a), over 30 nm in Figure 5b) to 62 nm in Figure 5c). For each dimer we recorded spectra at different analyzer angles which enabled us to resolve the polarization state of the light scattered off the particles.

For the touching dimer in Figure 5a), the intensity of the plasmon peak, which is centered at around 1.63 eV, is at maximum when the analyzer axis coincides with the dimer axis and takes its minimum value when the analyzer axis is oriented perpendicular to the dimer axis. The intensity distribution as function of the analyzer angle for the low energy mode is included as polar plot in Figure 5a). The plot confirms the dipolar character of the longitudinal mode, and we conclude that despite the short interparticle separation dipole-dipole coupling still dominates. In the case of conductively coupled gold nanoparticles a “shorting” of the dipole-dipole interactions was observed which resulted in the quadrupole as the dominating plasmon mode in nanoparticle pairs that have conductive overlap.⁶³ We think that for the hollow particles used in this study the PEG monolayer around the particles acts as an effective insulator that prevents a conductive path between the particles.

The higher energy mode of the dimer in Figure 5a) that peaks at around 1.80 eV is most prominent when the analyzer is orientated perpendicular to the dimer axis and is consequently assigned to the transverse plasmon mode. The spectra of the other dimers shown in the following were analyzed in a similar fashion, but for simplicity we only show the spectra for the analyzer settings closest to a parallel and perpendicular orientation with respect to the dimer axis in Figures 5b) and 5c).

In case of the touching dimer in Figure 5a), the longitudinal and transverse plasmon modes differ by $|\Delta E| = 170$ meV. For the dimer with an interparticle separation of 30 nm in Figure 5b), the longitudinal mode is centered at 1.75 eV and the transverse mode peaks at 1.82 eV. Due to the increased interparticle separation, the energetic stabilization of the longitudinal mode has decreased to $|\Delta E| = 70$ meV. In case of the dimer with an interparticle separation of 62 nm (Figure 5c)), we can no longer detect coupled plasmon resonances. The spectra recorded with an analyzer angle at 135° , corresponding to the plasmon mode perpendicular to the interparticle axis, is actually red-shifted compared with the spectrum recorded with the analyzer axis oriented along the interparticle axis (45°). We rationalize this observation by the fact that the interparticle coupling at this distance is weak and consequently structural features of the individual particles determine the recorded polarization dependent spectra. One of the particles has a slightly rod-like shape. The long particle axis is oriented perpendicular to the interparticle connection axis. The higher aspect ratio and the orientation of this particle can account for the red-shift of the plasmon resonance at analyzer angles perpendicular to the particle-particle connection axis, assuming that in hollow Ag-Au alloy rods the longitudinal mode red-shifts with increasing aspect ratio.

Our Ag-Au hollow particle preparations always contained some elongated hollow particles with aspect ratios between 1.3 and 1.7 (see Figure 6a)). As expected the longitudinal plasmon mode in these particles red-shifts with increasing aspect ratio. Figure 6b) contains an overview of the peak resonance energies of the longitudinal and transverse plasmon modes of all investigated Ag-Au alloy “hollow rods”. The resonance energies of the longitudinal modes

decrease linearly with aspect ratio A : $E_{rod}^{long} = 2.00 \text{ eV} - 0.30 \text{ eV} * A$. The transverse resonances are broadly spread but show an overall increase with increasing aspect ratio ($E_{rod}^{long} = 1.53 \text{ eV} + 0.21 \text{ eV} * A$). The touching dimer in Figure 5a) with an aspect ratio of approximately 1.7 has a longitudinal plasmon resonance energy of 1.63 eV, which is higher than the predicted value for a hollow rod with the same aspect ratio ($E_{rod}^{long} = 1.52 \text{ eV}$). In addition, for two other touching dimers with aspect ratios of 1.9 and 1.8 (see Figure S4 in the Supporting Information) the measured longitudinal plasmon resonances of 1.53 eV and 1.63 eV are also higher than the predicted resonance energies for continuous hollow rods with the same aspect ratio of $E_{rod}^{long} = 1.47 \text{ eV}$ and 1.53 eV , respectively. We find that the longitudinal plasmon resonances in touching HP2 particles have an average energetic bias of approximately 85 meV compared with rods with the same aspect ratio.

The spectral shifts between the transverse and longitudinal modes in touching dimers of HP2 particles range between 170 and 290 meV. The largest observed shift is comparable to what has been observed in touching solid gold nanoparticles of similar size,⁶⁴ but significantly smaller than the shift recorded in gold nanoshells around a silica core ($n_r = \sim 1.46$). For touching dimers of gold nanoshells with R values around 0.75 – as obtained through comparison of experimental spectra with boundary element calculations – a spectral shift of $|\Delta E| = \sim 680 \text{ meV}$ was observed. This strong red-shift was attributed to the synergetic effect of a strong nearfield coupling between the particles and a strong dielectric screening due to surfactants with a refractive index of $n_r = 1.42$ in the interparticle junction.⁴² Since in our experiments the pegylated particles were embedded in glycerin with $n_r = 1.47$ we expected a red-shift of similar magnitude. The coupling efficiency between two particles is largest when the energy levels of two particles match completely. The coupling decreases with increasing mismatch of the resonance energies.^{13,65} The hollow particles obtained through the galvanic exchange reaction used in this study showed a broad spread in their resonance energies (see Figure 2). An energetic mismatch of the plasmons in the hollow particles forming the individual dimers could account for the smaller shift observed in our study.

Conclusions

Through correlation of optical single particle spectroscopy with high resolution structural characterization of individual nanoparticles we have obtained a quantitative description of the optical properties of wet-chemically synthesized hollow particles with intrinsic size and shape heterogeneities. We investigated Ag-Au alloy hollow particles with average outer diameters of $53.0 \pm 4.0 \text{ nm}$ (HP1) and $96.9 \pm 8.1 \text{ nm}$ (HP2). We have experimentally mapped the resonance energy E_{res} and homogenous linewidth Γ_{hom} of the particles with their core-shell structure as obtained by TEM and measured the longitudinal and transverse plasmon modes in individual particle pairs. In the case of the HP1 particles, E_{res} decreases with growing R and the $E_{res}(R)$ relationship is best described by $E_{res}(HP1) = 2.52 \text{ eV} - 0.93 \text{ eV} * R$. The HP2 particles have slightly larger R values and the E_{res} values are overall red-shifted. The $E_{res}(R)$ relationship is approximated by: $E_{res}(HP2) = 2.77 \text{ eV} - 1.31 \text{ eV} * R$. The homogenous linewidth of the hollow particles ranges between $\Gamma_{hom} = 220 \text{ meV}$ to $\Gamma_{hom} = 420 \text{ meV}$. Γ_{hom} decreases with increasing R and increases linearly with E_{res} due to the increasing non-radiative damping through interband transitions at higher E_{res} . The longitudinal plasmon modes in hollow particles red-shift with regard to the transverse mode with decreasing interparticle distance; a maximum red-shift of the longitudinal mode of $|\Delta E| = 290 \text{ meV}$ is obtained for HP2 dimers with an interparticle separations below 1 nm. We found that the e-beam exposure during TEM inspection has a significant effect on the optical properties of the hollow particles – the intensity is decreased by a factor $> 20\times$, E_{res} was shifted by $\sim 200 \text{ meV}$ and Γ_{hom} increased by a factor

of > 2 . To avoid impairment of the optical properties it was mandatory to record the spectra of the particles prior to their structural characterization in the transmission electron microscope.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Correlation of optical spectroscopy with transmission electron microscopy. a) Dark-field optical image of a region containing a number of hollow particles. b) Scattering spectrum of Particle No. 5. c) TEM micrograph of the same area as in a) at 2,000x magnification. d) TEM image of particle No. 5 at high magnification (100,000x). The particle arrangement in a) serves as a “map” that facilitates the detection of the corresponding particles in the TEM micrograph c).

Figure 2.

Resonance Energy E_{res} versus the ratio R of inner and outer diameter for Ag-Au alloy hollow particles HP1 and HP2. Red and black dashed lines are linear fits for HP1 and HP2 particles, respectively. Green triangles: Peak plasmon resonance energies obtained from discrete dipole approximation (DDA)² simulations for Ag-Au alloy hollow particles with fixed outer diameter of 100 nm and assuming an Au mole fraction of 0.2 (see text).

Figure 3.

- a) Homogeneous linewidth Γ_{hom} as function of E_{res} for hollow particle batches HP1 and HP2.
 b) Homogeneous linewidth Γ_{hom} versus the normalized shell thickness $T = 1 - R$.

Figure 4.

- a) Scattering spectra of the same hollow particle before (green) and after (red) TEM inspection.
b) Histograms of the resonance energies (E_{res}) of ~50 randomly chosen hollow particles of the same HP2 batch before (green) and after (red) exposure to an e-beam.

Figure 5.

TEM micrographs (left) and scattering spectra (right) of hollow particle dimers. The spectra were recorded with an analyzer in the beam path in front of the detector allowing a polarization sensitive detection. The green and red arrows in the TEM micrographs indicate the recorded analyzer angles closest to a parallel (red) or perpendicular (green) orientation with respect to the interparticle axis. The corresponding spectra are included in red and green, respectively. a) Touching dimer (interparticle distance ≤ 1.0 nm). All scattering spectra of the analyzer sweep are included. b) Dimer with 30 nm interparticle separation. c) Dimer with 62 nm interparticle separation.

Figure 6.

a) Scattering spectra along the longitudinal (red) and transverse (green) axis of a rod-like hollow particle (aspect ratio $A = 1.6$). b) Resonance energies for longitudinal (E_{rod}^{long}) and transverse (E_{rod}^{trans}) plasmon modes as function of aspect ratio.