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Probing Silver Deposition on Single Gold Nanorods by Their Acoustic Vibrations

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Supporting Information

ABSTRACT: Acoustic vibrations of single gold nanorods coated with silver were investigated. We used single-particle pump–probe spectroscopy to monitor the silver deposition through the particle vibrations. Two vibration modes, the breathing mode and extensional mode, are observed, and the vibrational frequencies are measured as functions of the amount of silver deposited on single gold nanorods. The breathing mode frequency was found to decrease with silver deposition, while the extensional mode frequency was almost constant for silver shells up to 6 nm. The frequency changes agree with a model based on continuum mechanics and on the assumption of a uniform silver coating. The quality factors for the breathing mode and the extensional mode are hardly affected by silver deposition, indicating that the introduced interface between gold and silver contributes negligibly to the damping of the particle vibrations. Finally, we demonstrated that an atomic layer of silver can be detected using the particle acoustic vibrations.

KEYWORDS: Gold nanoparticles, core–shell nanoparticles, acoustic oscillations, damping, mass sensor, single particle

Plasmonic noble metal nanoparticles have attracted great attention due to their unique optical properties originating from the excitation of surface plasmon resonances. The plasmon resonance depends strongly on the size, shape, and composition of the particle, as well as on the medium in which the particle is embedded.1 This sensitivity combined with their large absorption and scattering cross sections have led to various applications of metal particles in areas such as sensing and imaging.2–4 Recent experiments have demonstrated that the properties of metal nanoparticles can be tuned further by the deposition of a second metal on their surface.5–9 Typically this deposition process is monitored through shifts of the surface plasmon resonance due to the changes in the shape and composition of the particle.5,10 However, the plasmon resonance is mostly sensitive to the shape of the particle, whereas the exact dimensions are difficult to obtain from the spectrum (the line width only depends weakly on the particle volume for intermediate particle sizes11). A prime example of this effect is the longitudinal plasmon of a subwavelength gold nanorod, whose frequency strongly depends on the aspect ratio (length/diameter) of the particle but only weakly on its volume.12,13

Recently, transient absorption spectroscopy has been employed as an alternative method to probe the deposition process via the acoustic vibrations of the coated particles.14–21 The acoustic vibration frequency depends strongly on the elastic constants of the material and on the dimensions of the particle.22,23 It therefore provides an optical method to monitor changes in the vibration frequencies during the coating process and yields information about the absolute particle size when the elastic constants are known. Several groups have reported on the acoustic vibrations of bimetallic particles with different coating thicknesses.14,20,21 However, these measurements were conducted on ensembles of nanoparticles and do not provide information on particle-to-particle variations or on possible additional damping mechanisms for example due to the creation of the metal–metal interface or the presence of crystal defects in the coating.

In this study, we investigated single gold nanorods as resonators to detect the deposition of silver through their acoustic vibrations. We observed both the breathing and the...
The white-light and pump–probe spectroscopy were performed as described earlier.\textsuperscript{3,22,25,26} White-light spectra of the particles were recorded in a reflection geometry.\textsuperscript{5,27} The white-light beam was focused onto the sample surface using a high-numerical-aperture objective (NA = 0.9). The reflected light from the glass–water interface was directed through a 50 μm pinhole and a band-pass filter and sent to a single-photon-counting avalanche photodiode (APD). A 20 × 20 μm\textsuperscript{2} raster scan image was recorded by scanning a piezoelectric stage and recording the reflected optical signal. The white-light spectrum of a single particle in the focus of the objective lens was recorded using a spectrometer equipped with a nitrogen-cooled charge-coupled device camera.

Acoustic vibrations of single gold nanorods were excited with the pulse train from a Ti:sapphire laser with a repetition rate of 76 MHz (wavelength 785 nm, ~300 fs pulse length). This pump laser beam was modulated by an acousto-optical modulator at a frequency of 400 kHz. The relative transmission change was probed by the frequency-doubled output of an optical parametric oscillator (OPO), tunable between 520 and 700 nm. The measured plasmon wavelength allowed us to choose the proper probe wavelength to observe both the breathing and the extension vibration modes in the time traces.\textsuperscript{22,26} The transmitted intensity of the probe beam was recorded with a fast Si-PIN photodiode, and a lock-in amplifier extracted the small change of the detected probe intensity \( \delta T \) at the modulation frequency. The vibration trace of the nanorods was constructed by recording \( \delta T(t) \) as a function of the time delay \( t \) between the pump and the probe pulses, controlled using a mechanical delay stage. In all measurements, the pump and probe–pulse energies were kept low to ensure that no melting or reshaping of the nanorods could occur, as judged by the white-light spectra before and after the pump–probe measurements.

Estimation of Silver Shell Thickness. The coating of silver on the surface of the gold nanorods was confirmed by measuring single-particle white-light spectra before and after incubation in the reaction solution. Examples of typical white-light spectra of the same gold nanorod after different successive incubation steps are shown in Figure 2a. In agreement with previous reports, the longitudinal plasmon of Au/Ag core–shell

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**Figure 1.** (a) Scanning electron micrograph of the gold nanorods dropcast on a silicon substrate. From such images, we extract an ensemble average size of 54 ± 3 nm in length and 25 ± 3 nm in width. (b) Scheme of the experimental setup described in the main text. The schematic in the dash-dot box illustrates how the pump and probe beams are focused on a single nanorod (not to scale). The white-light beam and the pump and probe pulses are focused by a high-numerical-aperture objective (NA = 0.9) on the sample surface. The transmitted probe pulses are collected by a lower-numerical-aperture objective (NA = 0.75) and directed to the appropriate detector. RS: aqueous reaction solution (4 mL of 20 mM ascorbic acid, 1 mL of 2 mM sodium citrate, 0.2 mL of 2 mM silver nitrate), AA: ascorbic acid (100 mM aqueous solution). LS: light sources including white-light, pump and probe pulses.
narrow nanorods was found to blue-shift as the silver coating grew thicker which is due to the decreased aspect ratio and the changed effective dielectric constant of the particle.\textsuperscript{12,13,28}

We now estimate the thickness of the silver shell based on the measured blue-shift of the longitudinal plasmon. Brioude et al. concluded that the Mie-Gans ellipsoid model was able to adequately account for the various peaks in the extinction spectra of gold nanorods.\textsuperscript{29} In this work, we used the Mie-Gans ellipsoid model because it allows us to calculate both the plasmon spectra of gold and Au/Ag core–shell nanoparticles. By using Mie-Gans ellipsoid model, we assumed that (1) the particle is embedded in a homogeneous environment with an effective refractive index, with no substrate present, (2) that the particle has a spheroidal shape, and (3) that the silver is deposited confocally onto the particle. The corresponding calculated spectra of gold and Au/Ag core–shell spheroids are shown in Figure 2b. The diameter of the gold particle (23 nm) was calculated from its breathing mode vibrational frequency (102 GHz) as shown in Figure 3.\textsuperscript{23} The length of the particle and the silver shell thickness were then varied to match the measured plasmon peaks as shown in Figure 2a. The above approximations introduce a maximum error of \(\sim 20\%\) in the estimation of the silver shell thickness; for more details see the Supporting Information, Figure S2. We find that the measured plasmon shift from 1.9 to 2.2 eV is caused by a silver shell of approximately 4.8 \(\pm 0.8\) nm in thickness. The calculated silver shell thickness is in reasonable agreement with reported transmission electron microscopy measurements,\textsuperscript{12,13,19} where a 3 nm silver shell on nanorods of 51 \(\pm 7\) nm in length and 17 \(\pm 3\) nm in width blue-shifts the plasmon resonance by \(\sim 0.3\) eV.\textsuperscript{19}

The evolution of the line width of the longitudinal plasmon with increasing silver shell thickness for several particles is shown in Figure 2c. The experimental curves were fitted with a Lorentz function yielding the plasmon energy and line width. Comparing the experimental white-light spectra with the theoretical calculations as shown in Figure 2b, the plasmon line width is well reproduced by considering the electron surface scattering and radiation damping in the gold core only (incorporated as a correction to the dielectric function of gold). This implies that the broadening is mainly caused by the interband transitions in gold which have an onset energy of \(\sim 2\) eV. We thus conclude that the gold–silver interface or crystal defects in the silver layer contribute little to the observed line-broadening.

**Theoretical Model for Breathing and Extensional Modes of a Core–Shell Nanorod.** Hu et al. used the classical theory of elasticity to derive expressions for the breathing and extensional frequencies of a slender nanorod composed of a single homogeneous material.\textsuperscript{23} Here, we extend that study and derive formulas for the fundamental breathing and extensional mode resonant frequencies of core–shell bimetallic cylindrical rods. These formulas are then compared to our single particle experimental measurements.

**Breathing Modes.** Consider an axisymmetric core–shell cylindrical rod of length \(L\), core radius \(R\) and a shell thickness \(h\). The ratio of shell thickness to core radius (\(\Delta = h/R\)) is arbitrary, and the rod length greatly exceeds its radius. The breathing modes correspond to purely radial deformations. Solving Navier’s equation in the core and shell regions, under the usual stress and displacement conditions at the boundaries, leads to the required result for the radial resonant frequency of the breathing mode (see the Supporting Information for derivation):

\[
\omega_{\text{br}} = \frac{\alpha_{\text{core}} \Omega}{R} \quad (1)
\]

where \(\Omega\) is a dimensionless eigenvalue that depends on the material properties of both the core and shell, and the shell thickness-to-core radius ratio; see eq S9 for its exact solution.

Given the complexity of the exact eigenvalue equation for \(\Omega\), we present asymptotic solutions in the limit of small and large shell thickness:

\[
\omega_{\text{br}} = \frac{\alpha_{\text{core}} \tau_{\text{core}}}{R} \{1 - A_1 \Delta + O(\Delta^2)\} \quad \Delta \ll 1 \quad (2a)
\]
Letter

The extensional radial resonant frequencies for the axial displacement are probed. The extensional mode at low frequency hardly changes with increasing silver thickness, while the frequency of the breathing mode decreases as indicated by the arrow.

Note that eq 6 implicitly assumes that the coating resides only on the sides of the rod; see Figure S3. Existence of a shell coating at the rod ends will decrease the resonant frequency in comparison to the predictions in eq 6, because the ends of the rod are stress-free. This effect is directly proportional to the coating thickness-to-rod length ratio and is thus of lower order than the side coating effect in eq 6. Given the rods used in this study possess an aspect ratio (length/width ~ 2), this end effect was included when comparing measurements to eq 6; that is, the rod length was increased by twice the coating thickness.

Measurements of the Acoustic Vibrations of Single Au/Ag Core–Shell Nanorods. Acoustic vibrations in metal nanoparticles are excited by two distinct mechanisms. First, the sudden surge in electron temperature created by the pump laser applies a pressure on the surface of the particle. Second, energy is then transferred from the electrons to the lattice through electron–phonon coupling on a time scale of several picoseconds. The particle is thus suddenly brought out of mechanical equilibrium and mechanical oscillations are launched. The acoustic oscillations cause periodic changes in the size and shape of the particle and can be probed with a light pulse with a wavelength close to the plasmon resonance. Figure 3a shows the delay traces of a single gold nanorod with different silver shell thicknesses. The corresponding white-light spectra of the same particle are displayed in Figure 2a. The delay traces show pronounced modulations arising from acoustic vibrations superposed on an exponentially decaying background due to the gradual cooling of the hot lattice. The delay traces were fitted with an exponential decay superposed on a sum of two damped oscillating terms:

\[
\frac{\delta T(t)}{T} = A_k \exp(-t/\tau_{\text{cool}}) + \sum_{k=\text{(ext,br)}} A_k \exp(-t/\tau_k) \cos(2\pi \nu_k t - \phi_k)
\]

where the first term represents the cooling of the particle and \(\tau_{\text{cool}}\) is the characteristic time for heat exchange between the crystal lattice and the environment. The oscillating term corresponds to two damped oscillation modes, with \(k = \text{extension (ext) or breathing (br)}\), each one with its own characteristic decay time \(\tau_k\), frequency \(\nu_k\), and phase \(\phi_k\). \(A_k\) and \(A_k\) are proportionality constants. Fitting eq 7 to the vibrational

\[
\omega_{\text{be}} = \frac{\alpha_{\text{shell}} \bar{\gamma}_{\text{shell}}}{R(1 + \Delta)} \left(1 + A_2 (1 + \Delta)^{-2} + O((1 + \Delta)^{-3})\right),
\]

where

\[
A_2 = \frac{A_1}{2} - \frac{\eta(\kappa_{\text{shell}}^2 - 1) - \kappa_{\text{core}}^2}{\kappa_{\text{shell}}^2 (\kappa_{\text{core}}^2 - 1) - \kappa_{\text{core}}^2}
\]

and \(\tau_z\) are the (homogeneous) eigenvalues satisfying:

\[
\tau_z J_0(\tau_z) = 2\kappa_{\text{shell}}^2 J_1(\tau_z)
\]

where \(Z\) is “core” or “shell”.

For the gold/silver nanorod studied, eq 2a predicts that the fundamental breathing mode frequency decreases as the shell thickness increases; this is in agreement with the exact solution, see Figure S4.

Extensional Modes. Derivation of the extensional mode frequencies of a core/shell rod follows along identical lines to that for a homogeneous rod. We again consider the case where the rod length greatly exceeds its radius, where the stress distribution is uniaxial for the extensional modes. The governing equation for the extensional displacement field of a core–shell rod is easily derived under such conditions, giving:

\[
\frac{d}{dx} \left( (E) A \frac{\partial u_{\text{ext}}}{\partial x} \right) - (\rho) A \frac{\partial^2 u_{\text{ext}}}{\partial t^2} = 0
\]

where \((E)\) and \((\rho)\) are the cross-sectional averages of the Young’s modulus and density, respectively, \(x\) is the axial coordinate, \(A\) is the total cross-sectional area of the rod, \(u_{\text{ext}}\) is the axial displacement field and \(t\) is time. Since eq 5 is identical in form to the governing equation for a homogeneous rod, the formulas for the extensional mode previously studied by Hu et al. apply here. The extensional radial resonant frequencies for a core–shell rod are therefore:

\[
\omega_{\text{ext}} = 2n + 1 \frac{\pi}{L} \sqrt{\frac{(E)}{\rho}}
\]
trace gives the extension and breathing frequencies as well as their respective damping times. The power spectral density of the traces is shown in Figure 3b, which exhibits two peaks due to the breathing and the extension modes. The frequency of the extensional mode is relatively constant, while the breathing mode shifts from 102 GHz to 79 GHz as the silver shell thickness increases from 0 nm to 4.8 ± 0.8 nm.

Figure 4a and b show the normalized resonant frequencies of the breathing and extensional modes of several gold nanorods as functions of the deposited silver layer thickness. Figure S5 gives the exact vibrational frequencies of each particle. The frequency of the extensional mode does not change significantly for silver layer thickness up to 6 nm. However, the frequency of the breathing mode decreases gradually with increasing silver shell thickness for all of the particles we studied.

Figure 4a and b also show predictions using the above breathing mode theory (full exact solution) and the theory for the extensional modes in eq 6. Gold nanorods synthesized by seed-mediated growth in the presence of silver ions are known to be single crystals with a [100] growth direction.32−34 The procedure we used to coat the gold nanoparticles studied here, with similar elastic properties and lower density, produces a similar effect to that of a homogeneous particle, albeit with quantitative differences. The presented rigorous model for the core−shell cylindrical rods captures this behavior accurately.

Breathing Modes. It is well-known that the breathing mode vibrational frequency of a homogeneous particle decreases with increasing size. This effect arises due to the particle mass increasing with the particle volume, while its stiffness increases linearly with particle size. Adding a coating to the gold nanoparticles studied here, with similar elastic properties and lower density, produces a similar effect to that of a homogeneous particle, albeit with quantitative differences. Specifically, the increase in frequency due to the shell coating is balanced approximately by the increase in length at the ends of the rod−this additional length increases the effective mass of the rod and hence lowers the frequency. In the model, we increased the rod length by twice the shell coating thickness. This overestimates the true effective mass because the density of silver is less than that of gold. Nonetheless, the agreement between measurement and theory is good. We refrain from a higher-level theoretical treatment of the extensional modes given the nonideal nature of the coating used in measurements; see above.

Figure 4c and d show the corresponding quality factor changes of breathing mode and extensional mode of gold nanorods coated with various amounts of silver shell as shown in Figure S5. The quality factors of bare gold nanorods deposited on a glass substrate and immersed in water are $Q_{br} = 23.5 ± 2.0$ and $Q_{ext} = 5.6 ± 0.7$ for the breathing mode and
extensional mode, respectively. The values are consistent with what we have recently measured.\textsuperscript{36} The quality factors of the breathing mode and the extensional mode after continuously coating a silver shell up to 6 nm are relatively constant. The introduced metal–metal interface and possible defects in the coating do not introduce significant additional damping of the vibrational modes. We thus conclude that both the plasmon damping and the vibrational damping show a negligible change due to imperfections in the coating.

**Monitoring the Atomic Layer of Silver Deposition.**

Errors in our experiments owing to the setup stability (causing drift of the particle out of the focus) and solvent exchange were both determined by measuring the same particle 10 times (see the Supporting Information, Figure S6). In the current studies, the standard deviations of the measured frequencies for the breathing mode and extensional mode are both relatively small and less than 0.3 GHz. The high accuracy in frequency measurements should enable us to detect very thin layers of silver by the acoustic vibrations. To verify this, we measured the vibrations of gold nanorods with a very thin layer of silver deposited (less than 1 nm). The silver deposition was controlled by the reaction time and estimated by measuring the white-light spectrum. The detailed results are shown in Figure 5.

The measured vibrational frequencies of several gold nanorods with a thin layer of silver are shown in Figure 5a and b, and the corresponding quality factors are shown in the Supporting Information, Figure S7. The breathing mode frequencies decrease upon deposition of a few atomic layers of silver, whereas the extensional mode frequencies do not show an obvious trend. These measurements show that it is feasible to detect an atomic layer of silver by changes in the particle’s acoustic vibrations, while other techniques, such as electron microscopy or X-ray scattering, are extremely challenging to apply in situ on the single-particle level. We note that shifts of the scattering profiles only yield the silver shell thickness if the volume of the individual particle is known from electron microscopy or atomic force microscopy images. The current all-optical method thus enables the in situ quantification of mass deposition in various environments. The sensitive high frequency acoustic vibrations of gold nanoparticles demonstrated in the present study could be developed for ultrasonic transducers with potential applications ranging from biological sensors through to sub optical wavelength acoustic imaging.\textsuperscript{37} Very recently, Fernandes et al. demonstrated that gold bipyramids can be used as mass sensors of silver atoms down to 40 attograms per gold nanoparticle in an ensemble measurement.\textsuperscript{38} By using single-particle spectroscopy, we are able to detect an atomic layer of silver, equivalent to \textasciitilde 10 attograms per gold nanoparticle. Our measurements and theoretical results show that the extensional mode is much less sensitive to silver deposition than the breathing mode. Therefore, the breathing mode would be the one to monitor in all sensing applications involving a similar distribution of deposited material.

**Conclusions.**

The acoustic vibrations of Au/Ag core–shell nanorods were investigated for varying amounts of deposited silver using single-particle pump–probe spectroscopy. Continuous silver coating of single gold nanorods was achieved by careful control of the synthesis parameters. We determined the silver thickness by combining single-particle absorption spectroscopy and acoustic vibrations of Au/Ag core–shell nanorods. Starting from single bare gold nanorods, the vibrational frequency of the breathing mode was found to decrease with increasing the silver thickness, whereas the changes of the extensional mode are much weaker. The measured vibrational frequencies are consistent with a model for core–shell bimetallic cylindrical rods based on continuum mechanics. The deposited silver on gold nanorods does not significantly damp the vibrational modes. We demonstrated that the acoustic vibrations provide an all-optical method to quantitatively detect an atomic layer of silver. Note that the presence of the substrate induces uncertainty (\textasciitilde 20\%) in the current experiments as it affects the vibrational frequencies (especially the extensional mode),\textsuperscript{22} the plasmon frequency, and the spatial distribution of silver that deposits on the particle surface. It would be interesting to perform future experiments with the particle trapped in optical tweezers, which will completely eliminate these effects as we have recently shown for pure gold nanorods.\textsuperscript{26}

**ASSOCIATED CONTENT**

3 Supporting Information

Stability of Au/Ag core–shell nanoparticles, estimation of the deposited silver shell thickness, model for the breathing mode frequency, the measured vibrational frequencies of the breathing and extensional mode, quality factors of the vibrations, and system errors. This material is available free of charge via the Internet at http://pubs.acs.org.
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