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Size and Nanocrystallinity Controlled Gold Nanocrystals: Synthesis, Electronic and Mechanical Properties

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The influence of nanocrystallinity on the electronic and mechanical properties of metal nanoparticles is still poorly understood, due to the difficulty to synthesize nanoparticles with controlled internal structure. Here, we report on a new method for the selective synthesis of Au nanoparticles in either single-domain or polycrystalline phase keeping the same chemical environment. We obtain quasi-spherical nanoparticles whose diameter is tunable from 6 to 13 nm with a resolution down to ≈0.5 nm and narrow size distribution (4-5%). The availability of such high-quality samples allows the study of the impact of particle size and nanocrystallinity on a number of parameters, such as plasmon dephasing time, electron-phonon coupling, period and damping time of the radial breathing modes.

1 Introduction

Structure-function relationship in nanoscience and nanotechnology is a topic of extreme interest, since at the nanoscale the thermal, mechanical and optical properties strongly depend on size, shape, composition, crystallinity and chemical interface.1-9 Chemists and physicists have made strong efforts to correlate the properties of nanoparticles (NPs) with their structures, with the ultimate goal to fabricate smart materials with a user-designed response.7 A notable example are the optical properties of gold and noble metal NPs.5,6,8,9 Chemical syntheses are nowadays available to rationalize the production of metal NPs with controllable size and shape.10-21 One of the most efficient methodologies for well-controlled chemical synthesis is the seeded-growth method, which allows a fine control of the gold NP growth on already-prepared seeds. However, the obtained NPs are usually dispersible in water and have size larger than 20 nm.11,12,17 Nonetheless, one parameter that is not yet well controlled is their nanocrystallinity, i.e. the amount of crystal defects inside the NP. Indeed, current syntheses are limited to the production of one form of nanocrystallinity, either single-domain or polycrystalline.12,18 The capability of synthesis of NPs with desired nanocrystallinity with narrow size and shape distribution in identical chemical environment (i.e. concentration and nature of reagents) is still lacking.22-27 Due to the limitations in synthesis control, only few studies have been reported concerning the role of nanocrystallinity on the properties of metal NPs.22-24,27,28 This difficulty of synthesis is attributed to the low stacking-fault energy of gold (≈40 mJ/m2), which implies that planar crystal defects in this material are easily formed.29 In NPs, the stacking faults often generate mirror planes that are named twins. This twinning process profoundly changes the internal structure of metal NPs and their overall shape. Indeed, the common polycrystalline forms of metal NPs are the multiply twinned particles (MTP), which are the decahedron and icosahedron.12,17,19,30 The former shape has 5 twins distributed on a quinary symmetry axis while the latter one has 30 twins distributed on 12 quinary symmetry axes. The single-domain shapes are well reproduced with the Wulff formula, which usually results in the truncated octahedron shape for fcc metals.31 It is known that the resistivity of metals decreases by increasing the amount of crystal defects, which act as scattering centers for the electrons.32 Consequently, the presence of twins should also modify the optical properties of gold NPs. Indeed, the localized surface plasmon resonance (LSPR) of NPs is a collective oscillation of their free electrons, which typically relaxes on the time scale of tens of femtoseconds.33-35 Following this initial ultrafast dephasing process, the photoexcited electrons lose their energy through several processes on different timescales, such as electron-electron36,39 (≈100 fs) and electron-phonon27,40-42 (≈1 ps) collisions. At longer delays, the photon energy deposited into the NPs leads to lattice expansion and to the generation of coherent acoustic vibrations with a few-ps period.6,22-25,38,43-48 These lattice vibrations can be monitored either in the frequency domain (using low-frequency Raman spectroscopy), allowing the observation of the NP quadrupolar vibration modes, or in the time domain (through pump-probe spectroscopy), enabling the investigation of the NP radial breathing modes (RBMs).26,44,49-51 How these ultrafast
relaxation processes in metal NPs are affected by nanocrystallinity is still a matter of debate. Here, we report on a new method for the synthesis of Au NPs with different nanocrystallinity, size tunable between 6 and 13 nm and narrow size distributions (4-5% rms diameter variation, as determined in the following). The quasi-spherical NPs are either in single-domain or polycrystalline phase, within the same chemical environment. The availability of such high quality samples allows us to study the effect of NPs size and nanocrystallinity on their electronic and elastic properties. Electron scattering on crystal defects is studied through the LSPR linewidth while the ultrafast optical response of these colloidal solutions is obtained via pump-probe experiments, which allow a detailed analysis of the NP electron-phonon coupling and coherent acoustic vibrations as a function of size and nanocrystallinity.

2 Experimental

2.1 Synthesis of the seed gold NPs.
The gold NPs used as seeds for the size- and nanocrystallinity-controlled growth are synthesized using a revisited method from the Stucky group. Briefly, 124 mg of chlorotriphenylphosphine gold (I) is dissolved in 25 mL of toluene with 500 µL of dodecanethiol. A solution containing 434 mg of tert-butylamine borane complex in 5 mL of toluene is used to reduce the gold precursor. The reaction takes place at 100°C and dark red color rapidly appears when the reducing agent is added.

2.2 Nanocrystallinity segregation.
The nanocrystallinity segregation was already reported in previous works. Before self-assembly process, the gold NP solution is washed with ethanol and the black powder is dispersed in toluene. In order to induce nanocrystallinity selection trough self-assembly, one has to avoid solvent evaporation. To that end, the resulting colloidal solution is left destabilizing in a closed flask. After one week, a black solid product is redispersed in hexane making the solution of single crystal seeds.

2.3 Seeded growth with different nanocrystalline seeds.
The growth of the seeds is induced in a solution of Au-oleylamine complex, produced by mixing, at 35°C, HAuCl4 in pure oleylamine at 11 mmol/L. After dissolution, the solution is yellow colored and freshly used. Then, 100 µL of colloidal solutions at 1.4 10^16 M of either single-domain or polycrystalline 5-nm NPs are mixed with the Au-oleylamine complex solution and the volume is completed to 2 mL with toluene. The seeded growth takes place at 90°C. During 6 hours, Au-oleylamine complex is slowly reduced on the seeds. The resulting nanocrystal size can be controlled by adjusting the gold complex concentration. After reaction, the NPs are washed with 2 mL of ethanol and redispersed in chloroform.

2.4 Electron microscopy.
The samples are prepared by depositing a drop of colloidal solution on a copper grid covered by an amorphous carbon film. The conventional TEM pictures are acquired with a JEOL 1011 at 100 kV. For the high-resolution experiments, a Jeol 2010 microscope is used at 200 kV. The size distribution and area of NPs are determined with the NIH ImageJ software by thresholding the pictures.

2.5 Wide-angle X-ray diffraction.
All the systems used to acquire X-ray diffraction patterns are under vacuum, from the emission of the copper anode to the detector. The detector is a curved photostimulable phosphor plate. After exposition, the film is scanned using a STORM 820 Molecular Dynamics scanner. The exposition is let running at least for 4 hours. The samples are made by evaporating the colloidal solution in a capillary tube with 100-µm diameter. The resolution of the peak width due to the experimental set up is determined by using the (102) and (201) rays of SiO2 micrometeric powder dispersed in oleylamine.

2.6 Pump-probe experiment.
The experimental setup used for the pump-probe studies has been described elsewhere. It is based on a regeneratively amplified Ti:sapphire laser (Coherent, Libra) producing 100-fs, 4-mJ pulses at 800 nm wavelength and 1-kHz repetition rate. A portion of this beam is frequency doubled to obtain the 400-nm pump pulses. Another fraction of the pulse is focused in a 2-mm-thick sapphire plate to generate a broadband single-filament white-light continuum (WLC) that acts as a probe after passing through a delay line. The visible portion of the WLC, extending from 430 nm to 760 nm, is overlapped with the pump beam on the sample. The transmitted/reflected light is dispersed on an optical multichannel analyzer equipped with fast electronics, allowing single-shot recording of the probe spectrum at the full 1-kHz repetition rate. By changing the pump-probe delay we record two-dimensional maps of the differential transmission (∆T/T) signal as a function of probe wavelength and delay. Our setup achieves, for each probe wavelength, sensitivity down to ≈10^-8. Temporal resolution (taken as full-width at half-maximum of pump-probe cross-correlation) is ≈180 fs over the entire probe spectrum.

3 Results and Discussion.
The synthesis starts by producing a mixture of single-domain and polycrystalline 5-nm NPs (Fig. 1a), revisiting the organometallic method developed by Stucky et al. It has been demonstrated that nanocrystallinity segregation occur by letting such a colloidal solution under toluene saturation during 7 days. Indeed, low frequency Raman spectra show that the polycrystalline NPs are still dispersed in the solution whereas single-domain self-assemble into a 3D superlattice during the destabilization of the colloidal solution (Fig. S1). The resulting superlattices exhibit orientational ordering which implies an atomic alignment between the single-domain NPs. This crystallographic register explains the stronger interactions between single-domain NPs compared to the polycrystalline ones, induced by nanocrystal facet-to-facet geometry. Thanks to this crystallinity segregation process, we are able to selectively synthesize 5-nm single-domain and polycrystalline NPs, both dispersed in hexane (Figs. 1b, 1f). Such NPs are used
Fig. 1 (a) A schematic image showing the formation of gold NPs with tunable size and nanocrystallinity, the polycrystalline NPs are represented in red and single-domain in blue with straight lines. (b-e) TEM images of NPs synthesized using polycrystalline seeds, (b) 5.6 nm; (c) 6.8 nm; (d) 9.6 nm and (e) 12.7 nm. (f-i) TEM images of NPs synthesised using single-domain seeds, (f) 5.9 nm; (g) 6.7 nm; (h) 9.6 nm and (i) 13.2 nm. The scale bars are 20 nm.

as seeds to selectively grow single-domain or polycrystalline NPs differing by their sizes (Fig. 1a). The growth of the seeds is induced in a solution of Au-oleylamine complex. The gradual Au input on the seed surface avoids any nucleation of new NPs. In this way, the obtained polydispersity of NP diameters is low (3-7%), as shown in figures 1b-1i and in Supporting Information (Fig. S2 and S3). Moreover, the size distributions display Gaussian profiles, thus confirming that the growth of the seeds is homogeneous and it cannot be attributed to sintering or Ostwald ripening of NPs, which usually lead to a lognormal distribution (see Supporting Information, Fig. S2 and S3). The mean NP diameter is controlled by the Au complex concentration in the reaction solution, determined by the volume of Au-oleylamine input. The determination of the nanocrystallinity purity is impossible with the various techniques used in this study since the XRD measurements provide an average response of the nanocrystals. Moreover, one has to take into account that crystallinity segregation can occur during the monolayer formation on the TEM grid and therefore this effect will distort the purity percentage due to the local probing area. This makes the determination of the purity percentage impossible. However, the crystallinity purity of the seeds has been investigated by low frequency Raman

Fig. 2 Typical mean diameter of single-domain (blue squares) and polycrystalline (red circles) NPs as a function of gold complex concentration during the seeded growth.
The nanocrystallinity of Au NPs was investigated by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Figure 3a shows typical diffraction profiles of \{111\} and \{200\} Au lattice planes. The blue and red curves are obtained from 13.2-nm and 13.1-nm NPs synthesized from single-domain and polycrystalline seeds, respectively. The diffraction profiles of the other NPs with different diameter is shown in the Supporting Information (Fig. S4 and S5). The crystallite size, \(D_{\text{XRD}}\), is determined from the Scherrer formula\(^\text{52}\) using the broadening of the peak extracted from a pseudo-Voigt fit. For NPs produced using single-domain seeds, Figure 3b shows a good agreement between the \(D_{\text{XRD}}\) determined from both \{111\} and \{200\} reflections and the NP diameter determined by TEM (\(D_{\text{TEM}}\)). This indicates that the overall populations are single-domain without any anisotropy in the crystallite shape (quasi-sphere). The HRTEM images (Figs. 3c, 3f) show the lattice fringes of single domain NP and confirm the nearly spherical NP shape with small flat facets. In the case of NPs synthesized with polycrystalline seeds, the crystallite size is smaller on the \(\langle 200 \rangle\) directions compared to the \(\langle 111 \rangle\), and both are smaller than \(D_{\text{TEM}}\). This anisotropic shape of the crystallites is confirmed by the HRTEM images, where two main MTPs with tetrahedral sub-units are observed: decahedron (Figs. 3d, 3g) and icosahedron (Fig. 3e). As with single-domain NPs, the edges of the polycrystals are round (Fig. 3g). The oxidative etching of oleylamine in presence of \(O_2\) on Au NPs is well known.\(^\text{57}\) This etching process is reported to select single-domain instead of polycrystalline NPs via dissolution of Au preferably on crystal defects. Here, the solutions are already with selected nanocrystallinity and no selective etching is observed. Whatever their nanocrystallinity, the NPs are etched on their vertices and edges during their growth. This results in a nearly...
spherical shape with distribution of vicinal surfaces between their small facets. In order to characterize a possible shape variance between single-domain and polycrystalline NPs, the circularity “c” of the Au NP is defined as:

\[ c = \frac{A_{NP}}{A_{disc}} \]  

with \( A_{NP} \) the area of the NP projection on TEM pictures and \( A_{disc} \) the area corresponding to the perfect circumscribed disc. The larger diameter of the NP projection, also called Feret diameter, is used to determine A. Figure 3h shows the circularity distribution histograms of both single-domain (blue) and polycrystalline (red) 6.6 nm NPs; they are nearly fully overlapped. From this we conclude that both single-domain and polycrystalline NPs can be seen as quasi-spheres. Similar circularity distributions for NPs with different diameter are shown in the Supporting Information (Fig. S6). By fitting the XRD pattern with a pseudo-Voigt function, it is possible to extract the Lorentz factor and determine if the peak broadening is mainly Lorentzian or Gaussian (see Table S1 in the Supporting Information). The main contribution for polycrystalline NPs is clearly Lorentzian indicating a larger crystallite size distribution due to the different tetrahedral sub-units size of icosahedron and decahedron. In the case of single-domain NPs, the Gaussian profile reveals the narrow crystallite size (i.e. NP size) distribution. Hence, starting from Au seeds with controlled nanocrystallinity, it is possible to synthesize nearly spherical NPs with tunable diameter, narrow size distribution and with the same chemical environment.

3.2 Localized Surface Plasmon Resonance.

The NPs coated with dodecanthiol are dispersed in chloroform after synthesis. We have recorded the linear absorption spectra of single-domain and polycrystalline NPs with different sizes. Figure 4a shows representative examples for NPs with 6.6 nm diameter; the spectra are dominated by the LSPR absorption band at 527 nm. As already observed for 5 nm nanoparticles,\(^5\) for any size in the 6 to 13 nm range, the LSPR band of polycrystalline NPs is characterized by a weaker intensity and larger linewidth compared to single-domain NPs having the same average size. Inset of Figure 4a confirms that in the size range studied here, according to the well-known Fröhlich formula, the LSPR position does not depend on the NP diameter, so that the influence of the narrow size distribution on the broadening of the LSPR band is negligible. The optical properties of Au NPs larger than 5 nm can be well represented with a classical approach,\(^5\) in which the LSPR linewidth is related to the electronic scattering rate and given by:

\[ \Gamma = \Gamma_0 + \frac{A_{vF}}{R} \]  

where \( \Gamma_0 \), A, \( v_F \) and R are the intrinsic electron scattering rate, a constant dependent on the dielectric constant of the medium, the Fermi velocity of electrons and the NP radius, respectively. From the circularity data shown above, to a first approximation, we can assume that the NPs are spherical. The intrinsic electron damping constant is represented by the different electron collision events which are defined by the Matthiessen law\(^5\) and the absorption due to the interband transition.\(^5\) Indeed, since the LSPR of Au NPs partly overlaps with the interband transition due to its short-wavelength threshold (\( \approx 540 \) nm), one has to take it into account in the following description:

\[ \Gamma = \Gamma_0 + \frac{A_{vF}}{R} \]  

where \( \Gamma_0 \), \( A_{vF} \), and R are the intrinsic damping times due to the scattering of the electrons on phonons, electrons and lattice defects (e.g. point defects, dislocations and grain boundaries), respectively. The last term describes the absorption due to interband transition where \( \omega_{\text{LSPR}} \) is the LSPR frequency, \( \omega_0 \) the plasma frequency of the metal and \( \varepsilon_2^b \) is the imaginary part of the interband contribution of bound electrons to the dielectric function.\(^5\) Note that due to the size dependences of \( \tau_{vF} \) and \( \tau_{c-e} \), \( \Gamma_0 \) is different from the bulk value. However, since the \( \tau_{vF} \) and \( \tau_{c-e} \) size dependences mostly concern NPs with diameter below 5 nm, it can be neglected in our case. The experimental LSPR absorption band is fitted with the superposition of a Lorentzian function and a linear decay that takes into account the absorption due to interband transitions (see Supporting Information, Fig. S7). From such analysis we extract the LSPR linewidth (\( \Gamma \)) of our samples. Figure 4b shows the relation between \( \Gamma \) and \( R \).
intrinsic scattering rate \( \Gamma_0 \) and of the constant \( A \), which are 11.3.fs\(^{-1} \), 0.19 and (8.6.fs\(^{-1} \), 0.22 for single-domain and polycrystalline NPs, respectively. The difference in the linewidths cannot be attributed to the chemical interface damping, since the NPs are synthesized in the same chemical environment. The similarity of the constant \( A \) for both nanocrystalline phases confirms that the chemical environment and consequently the dielectric constant of the medium remains unchanged, suggesting comparable electron-surface scattering processes. Since \( \Gamma_{\text{LSPR}} \) does not depend on the nanocrystal size (inset Figure 4a), the absorption due to the interband transition is similar for single-domain and polycrystalline NPs. Then, the observed difference in \( \Gamma_0 \) (11.3.fs\(^{-1} \)) and (8.6.fs\(^{-1} \)) between single-domain and polycrystalline NPs is attributed to crystal defects increasing the scattering rate, as shown in Eq. (3). In particular it has been shown that the plasmon linewidth of polycrystalline gold NPs is strongly affected by the grain size.\(^{59} \)

We conclude that the collection of polycrystalline NPs have intrinsic dephasing rates around 20% higher than single-domain NPs due to the electron scattering on their crystal defects. This result reveals the important and often neglected role of twins in determining the LSPR linewidth. Indeed, the main parameter that is used to calculate the NP optical response obtained with single-particle spectroscopy is the surface scattering parameter, \( \Lambda \).\(^{55,58} \) However, the values of this parameter are often different from one NP to the other while the crystal defects can also contribute to the LSPR broadening and have to be taken into account.

3.3 Femtosecond Broadband Pump-probe Measurements.

The availability of high-quality size-controlled samples, with either poly or single-crystalline phase, allows us to study the effect of size and nanocrystalinity on the electronic and vibrational dynamics of gold NPs. We performed pump-probe measurements of the NPs dissolved in chloroform in a 1 mm optical-path cuvette. The sample was excited at 400 nm and the differential transmission \((\Delta T/T)\) signal was measured over the entire visible spectral region using a white-light femtosecond pump-probe system. The measurement was performed by subtracting a slowly varying background from the transient spectra after photoexcitation: an example of the recorded \( \Delta T/T \) signal is shown in panel (b).\(^{46} \)

We isolate the oscillatory component of the signal by subtracting the slowly varying relaxation dynamics for each probe wavelength. The coherent oscillations on the two sides of the plasmonic resonance obtained by subtracting the slowly varying exponential decays to the map in panel (b) period of the fundamental RBM in small nanoparticles, this expansion impulsively launches coherent oscillations that are coupled to the optical response of the sample through a periodical shift in the position of the LSPR peak.\(^{47} \) In the case of Au spherical NPs they arise from periodical variations of the volume and, consequently, of the carrier density which directly affects the plasma frequency. An example of the measured coherent oscillations in the 11.6 nm diameter single-domain NPs is highlighted in Figure 5, where in panel (c) we plot a close up of the recorded \( \Delta T/T \) signal (shown in panel b), for delays longer than 6 ps (to remove the initial fast thermalization process). We isolate the oscillatory component of the signal by subtracting the slowly varying relaxation dynamics for each probe wavelength. It is worth noting that the amplitude of the oscillation is larger at longer wavelengths (540-570 nm) with respect to the plasmonic peak (~525 nm) and a \( \pi \) phase shift occurs for wavelengths at different sides of the LSPR,\(^{46} \) as expected from oscillations arising from a periodic shift of an optical resonance. In the following, we will first investigate the electron-phonon scattering dynamics, which occur during the first \( \approx5 \) ps after excitation, and then we will focus on the analysis of the coherent oscillations on the longer timescale.

3.4 Electron-Phonon Scattering

It is known that the time constant for the electron-phonon scattering increases linearly with the excitation fluence: \(^{41} \) this can be explained in the framework of the two-temperature model given that a higher pump intensity creates a higher initial electronic temperature that is directly reflected in the relaxation time constant.\(^{47} \) Indeed, at low pump power, the electron-phonon scattering time constant is given by

\[
\tau_{e-ph} = \gamma (T_0 + \Delta T)/g
\]

where \( \gamma \) is the electron heat capacity constant, \( g \) is the electron-phonon coupling constant, \( T_0 \) and \( \Delta T \) are the ambient temperature and the pump-induced temperature increase, respectively. Among the parameters that can affect the electron-phonon scattering rate, the nanocrystallinity of the sample is believed to play a fundamental role but still experiments in this...
Fig. 6 Effect of the nanocrystallinity on the electron-phonon scattering. (a) ΔT/T dynamics (data points) for single-domain NPs with 10.6-nm diameter excited at 400 nm and corresponding fitting (solid lines) obtained considering 180-fs temporal resolution, a fixed electron-electron scattering time constant of 340 fs and an electron-phonon scattering time constant as a free parameter. Pump fluences: 12.7 µJ/cm² (diamonds and red curve), 140 µJ/cm² (circles and blue curve, scaled down by 8.7 times to normalize the trace to the low-fluence data) and 267 µJ/cm² (squares and green curve, scaled down by 15.9 times). The electron-phonon scattering time constant is kept as a free parameter. (b) Extracted electron-phonon scattering time constant as a function of pump fluence for both single-domain (blue squares) and polycrystalline (red circles) NPs with 10.6-nm diameter; solid black line is a linear fit to the data (intercept at τ_{eqph}^0=625 fs; slope 1.96 fs cm²/µJ).

Let’s now turn to the study of the coherent oscillations for Au NPs differing by size and nanocrystallinity. In the case of phonon scattering dynamics, as the two datasets are performed fluence-dependent measurement on Au NPs of the same size that only differs in terms of their nanocrystallinity. In Figure 6(a) we show the measured (data points) ∆T/T dynamics for single-domain NPs (blue squares and green curve) and polycrystalline NPs (red circles) NPs with 10.6-nm diameter; solid black line is a linear fit to the data (intercept at τ_{eqph}^0=625 fs; slope 1.96 fs cm²/µJ). This value, in good agreement with previous reports, reflects the fundamental RBM energy and further confirms the quality of our results. Very similar results were obtained for another couple of samples consisting of single-domain and polycrystalline NPs with 7.7 nm diameter.

3.5 Radial Breathing Mode Oscillations

Let’s now turn to the study of the coherent oscillations for Au NPs differing by size and nanocrystallinity. In the case of spherical NPs, the vibrational modes can be accurately described as those of an elastically isotropic homogeneous sphere and time-domain experiments mainly probe their fundamental RBM, due to isotropy of the thermal excitation. Following this description, the computed frequencies of the RBM are expected to be almost identical for single-domain and polycrystalline samples but experimental results in this direction are still controversial. Strong variations were found between single-domain and polycrystalline structures in the case of silver and hollow gold nanospheres while no significant effect was observed in 7-nm Cu and 5-nm Au NPs.

In Figure 7 panels (a) and (b) we show the RBM oscillations detected at 550 nm probe wavelength for the 11.6 nm diameter spherical NPs with different crystallinity (data points). Similar results for the all the other NPs are reported in the Supporting Information (Fig. S8 and S9). The amplitude of the oscillations rapidly decays in time and after 6-7 periods it vanishes below the sensitivity of our measurements. The decay can be attributed mainly to two mechanisms: (i) intrinsic damping of the RBM caused by energy dissipation, giving rise to an homogeneous broadening and to an exponential decay in time e^{-t/τ}; (ii) dephasing of the oscillations due to inhomogeneous broadening related to the size distribution of the NP, which translates into a superposition of oscillators with different period, giving rise to a e^{-t/τ} decay profile. Both methods...
provide very good fits of our data (see Supporting Information, Fig. S8 and S9), with minor differences in the residuals. Anyway, we can exclude a pure inhomogeneous broadening related to the size distribution of the NPs for the following reasons. If the latter was the only cause of the damping of the RBM, the standard deviation $\sigma_0$ of the NP diameter distribution extracted from the pump-probe data would be larger than that estimated from TEM images (see Fig. S2 and S3 in the Supporting Information). In fact, knowing the average diameter $\bar{D}$ of each sample, from the fits of the pump-probe data we can extract the oscillation period $T$ and the time constant $\tau$ of the Gaussian decay, so that the standard deviation $\sigma_0$ can be evaluated from the equation $^6$

$$\sigma_0 = \frac{\bar{D}T}{\sqrt{2\pi}} \quad (5)$$

The results are plotted in the Supporting Information (Fig. S10(a)), together with those obtained from the TEM images, which are an overestimation of the real standard deviation because they are very close to the resolution of the instrument. This allows us to conclude that the major contribution to the damping of the RBM oscillation is the intrinsic damping caused by energy dissipation, thanks to the extremely high purity of the samples (see also the polydispersity extracted from the data in Supporting Information Fig. S10(b)). In the following we therefore consider the results obtained from the fits using an exponential decay. The extracted periods of oscillation $T$ and decay time constants $\tau$ are reported in Fig. 7(c) and 7(d) as a function of NP diameter for single-domain (blue squares) and polycrystalline (red circles) NPs. The period of oscillation $T$ increases linearly with the sphere size for both sets of samples. In accordance with theoretical predictions,$^2$ our experiments show that the RBM period is not affected by the nanocrystallinity: the data points in Figure 7(c) lie on the same straight line. The linear fit of the entire dataset (with intercept set to zero) gives a slope of $\frac{T}{D} = 330 \text{ fs/nm}$, which is in good agreement with the inverse of the longitudinal speed of sound in gold $\frac{1}{v_s} = 310 \text{ fs/nm}$. This suggests that the nanoscale mechanical properties of the NPs, in particular the Young modulus which determines the speed of sound, are not significantly affected by nanocrystallinity. From the analysis of Figure 7(d) we can conclude that the two datasets lie onto straight lines with different slope: $\frac{\tau_s}{D} = 930 \text{ fs/nm}$ for the single-domain NPs (blue squares) and $\frac{\tau_p}{D} = 670 \text{ fs/nm}$ for the polycrystalline ones (red circles). The quality factors associated with the two crystallinities are then $Q_s = \pi \frac{\tau_s}{T} \approx 9$ for the single-domain and $Q_p = \pi \frac{\tau_p}{T} \approx 6$ for the polycrystalline NPs.

**Conclusions**

In this paper we described a novel synthesis method that allows the control of golden NP size and nanocrystallinity using the same chemistry (i.e. nature and concentration of the reagents). We obtained either single-domain or polycrystalline NPs in the size range of 6-13 nm diameter with narrow size distribution. The oxidative etching of oleylamine/O$_2$ permits the formation of quasi-spherical NPs for both nanocrystallinities. The availability of such highly controlled samples gave us the unique opportunity to investigate the influence of both size and nanocrystallinity on the electronic, thermal and mechanical properties of the NPs. We observed that the presence of the twin defects leads to an increase by 20% in the LSRR linewidth compared to the single-domain NPs. This broadening is attributed to an additional term in the intrinsic electron damping time due to the scattering of electron on the defects. Differently from plasmons, no influence of nanocrystallinity on electron-phonon equilibration dynamics is observed, suggesting that twins do not significantly enhance the electron-phonon scattering processes. Finally, the frequency and damping time of impulsively excited acoustic vibrations of the NPs are directly probed in the time domain. We show that the elastic properties of the NPs, which determine the speed of sound and thus the vibration period, are not significantly affected by the nanocrystallinity; on the other hand, the damping of the vibrations, through dissipation of the mechanical energy to the environment is sensitive to defects and twins. The damping of the RBM acoustic oscillations can thus be taken as a fingerprint of the nanocrystallinity of the NPs.

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**Notes and references**

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**References**

Graphical abstract

Controlled synthesis of gold nanocrystals differing by their sizes and nanocrystallinity allow study of their acoustic and electronic vibrations.