Morphology-Dependent Coherent Acoustic Phonon Vibrations and Phonon Beat of Au Nanopolyhedrons

Li Wang, Shohei Takeda, Ryota Sato, Masanori Sakamoto, Toshiharu Teranishi, and Naoto Tamai

ABSTRACT: Coherent acoustic phonon vibrations of Au nanopolyhedrons, including nanocubes, nano-octahedrons, and nanocuboctahedrons, in aqueous solutions and poly(vinyl alcohol) (PVA) films, were investigated using transient absorption (TA) spectroscopy combined with finite element analysis based on continuum elastic theory. In each type of nanopolyhedron, two vibrational modes with similar quality factors (Qs) and phases were observed, suggesting that both were induced by thermal expansion. The low-frequency vibrational mode represents a tip-to-tip displacement in each nanopolyhedron, whereas the high-frequency mode is the breathing vibration of the whole particle and reveals morphology dependence, displaying a face-to-face displacement in nanocuboctahedrons, an edge-to-edge displacement in nano-octahedrons, and a combination of face-to-face and edge-to-edge displacements in nanocubes. Moreover, a clear phonon beat was identified in the two vibrational modes of the nanocuboctahedrons. Our experimental results provide a possible application of morphology-controllable metal nanoresonators.

INTRODUCTION

Metal nanoparticles have unique optical properties such as localized surface plasmon resonance (LSPR) and surface-enhanced electromagnetic (EM) fields. Their potential applications have been explored as light collectors for solar cells and photocatalysis, optical probes for nondestructive spectroscopy, contrast agents and nanoelectrodes for photothermal therapies, and nanoresonators for optomechanical devices. The interactions between metal nanoparticles and EM fields, which can be studied by time-resolved spectroscopy, motivate all applications. With light irradiation of metal nanoparticles, electron distribution near the Fermi level is suddenly disturbed, including high electron temperatures via electron−electron scattering. Hot electrons and lattice relaxation by electron−phonon coupling follow two temperature models. During the entire process, the plasmon band can be affected by the electron distribution and particle size, which originate from impulsive electron gas and coherent acoustic phonon vibration, respectively. In the transient absorption (TA) measurements, the highly symmetrical phonon vibration modes can be detected. The fundamental breathing mode and extensional mode have been observed in regular Au nanostructures, such as nanospheres and nanorods, in accordance with analytical expressions based on continuum elastic theory. However, acoustic vibrational modes of shape-controlled metal nanopolyhedrons, representing high catalytic activities by high-energy surface engineering and high performances in surface-enhanced spectroscopy as plasmonic hot spots, have been less reported. Two vibrational modes were detected for large Ag nanocubes, assigned to the breathing mode induced by lattice thermal expansion and the nontotal symmetric mode by impulsive electron pressure. For Au nano-octahedrons, the extensional mode was detected by micro-Brillouin spectroscopy and four-wave mixing (FWM). Recently, single-particle time-resolved spectroscopy of quasi-spherical Al nanocrystals revealed one size-dependent vibration frequency in faceted samples and two distinct frequencies in triangularly shaped samples. Owing to their different sizes and morphologies, metal nanopolyhedrons can provide multi-oscillation frequencies as controllable optomechanical resonators. The different vibrational modes of the nanopolyhedrons could be classified by a combination of TA experiments and numerical investigations.

In this study, we performed TA measurements of Au nanocubes, nano-octahedrons, and nanocuboctahedrons in aqueous solutions, as well as poly(vinyl alcohol) (PVA) films. Coherent acoustic phonon vibrations were observed in the three Au nanopolyhedrons, representing multi-vibrational modes in which the phonon beat was clearly detected in Au nanocuboctahedrons. The shape and size dependences are discussed with numerical simulations using the finite element method (FEM). Our experimental results suggest that
controllable optomechanical properties could be achieved by metal nanostructure morphology engineering.

RESULTS AND DISCUSSION

Figure 1a–c show a typical transmission electron microscopy (TEM) image of Au nanocubes and scanning electron microscopy (SEM) images of Au nano-octahedrons, and nanocuboctahedrons, respectively. The side lengths ($L_s$) were estimated from $\sim$200 particles in each case. The histograms of $L_s$ and their standard derivations are shown in Figure S1 and Table 1. Plasmon resonances of Au nanocubes, nano-octahedrons, and nanocuboctahedrons are affected slightly by the particle sizes and morphologies, as illustrated in Figure 1d. The peak wavelengths of the extinction spectra of the three samples are located at 541, 558, and 533 nm, respectively.

Figure 2a shows the TA spectra of the Au nanocubes at certain delay times after an 83 $\mu J/cm^2$ excitation by 400 nm femtosecond laser pulses. TA spectra exhibited a bleach peak and positive absorption signals at the two sides of the bleach peak, induced by the broadening and red-shift of the plasmon band originating from the heating of the electrons and lattices by the excitation pulses. The peak wavelength of the bleach signal was initially located around the plasmon peak of the nanocubes (542 nm at a delay time of 0 ps), then blue-shifted within the first oscillation (533 nm at 12 ps), and finally

Table 1. Amplitude $A_0$, Phase $\varphi$, Frequency $f_0$ ($=1/T_0$), and Quality Factor $Q$ of the Oscillation Dynamics of the Bleach Wavelengths and Calculated Vibration Frequency $f_0^{\text{FEM}}$

| mode    | $A_0$ (nm) | $\varphi$ (rad) | $f_0$ (GHz) | $f_0^{\text{FEM}}$ (GHz) | $Q$ $(2\pi T_0/2)$ |
|---------|------------|-----------------|-------------|--------------------------|------------------|
| cube    | $L = 56 \pm 3$ nm | I 0.6 $\pm$ 0.2 | -0.04 $\pm$ 0.01 | 29.9 $\pm$ 0.6 | 27.8 | 16.7 |
|         |            | II 1.7 $\pm$ 0.2 | 0.00 $\pm$ 0.03 | 46.8 $\pm$ 0.3 | 42.7 | 16.5 |
| octahedron | $L = 58 \pm 2$ nm | I 1.3 $\pm$ 0.2 | 0.10 $\pm$ 0.06 | 30.0 $\pm$ 0.2 | 30.8 | 19.7 |
|         |            | II 0.8 $\pm$ 0.2 | 0.20 $\pm$ 0.07 | 52.9 $\pm$ 0.3 | 52.3 | 23.1 |
| cuboctahedron | $L = 37 \pm 3$ nm | I 1.0 $\pm$ 0.1 | 0.05 $\pm$ 0.03 | 51.4 $\pm$ 0.1 | 43.2 | 22.7 |
|         |            | II 1.2 $\pm$ 0.1 | 0.09 $\pm$ 0.03 | 57.8 $\pm$ 0.1 | 51.3 | 21.2 |
oscillated at around 535 nm. The decay profiles at 516 and 558 nm located at the two sides of the bleach band are plotted in Figure 2b. After electron–phonon scattering for several picoseconds, π out-of-phase oscillation was observed in the decay profiles, due to a plasmon spectral shift mainly induced by coherent acoustic phonon vibration. With Gaussian fitting of the TA spectra, the dynamics of the bleach peak wavelength in Figure 2c are more representative of the coherent acoustic phonon vibration of the ensemble. The oscillation in Au nanocubes consisted of two vibrational modes, determined by fast Fourier transform (FFT) of the modulated portion in the oscillation dynamics, as shown in Figure 2d, labeled “I” and “II.”

The dynamics of the bleach peak wavelength \( \lambda_t \) were fitted to the following equation

\[
\lambda_t = A_{e-p} \exp\left(\frac{-t}{\tau_{e-p}}\right) + \sum_{v=I,II} A_v \exp\left(-\frac{t}{\tau_v}\right) \cos\left(\frac{2\pi t}{T_v} - \phi_v\right) + A_{th} \exp(-t/\tau_{th}) + \text{baseline}
\]

(1)

where the two exponential factors describe electron–phonon coupling and thermalization of lattices with the surroundings, and the two damped cosine functions represent two coherent acoustic phonon vibrational modes. \( \tau_{e-p} \) and \( \phi_v \) are the amplitude of the spectral shift, the time constant of decay and damping, the period, and the phase of vibrational modes, respectively. The baseline is the central wavelength of bleach peak oscillation.

The fitting results are listed in Table 1. The periods (frequencies \( f_v \)) for the Au nanocubes are 33.4 ± 0.6 and 21.4 ± 0.1 ps (29.9 and 46.8 GHz), in good agreement with the two vibrational modes simulated by FEM with bulk elastic properties (27.8 and 42.7 GHz). The two phonon modes have less phase difference (π/25) and similar quality factors (Qs), different from the reported results for Ag nanocubes.

In the case of Ag nanocubes (larger than 50 nm), two vibrational modes were also detected, representing π/2 out-of-phase oscillation and different Qs, assigned to different mechanisms of impulsive electron pressure and lattice expansion. For our Au nanocubes, the two vibrational modes were induced by the same mechanism, lattice thermal expansion. In the TA measurements, the highly symmetric acoustic vibrational modes can be detected. The two vibrational modes of the Au nanocubes might be breathing modes, similar to the predominant mode in Ag nanocubes. Moreover, TA measurements of Au nanocubes in PVA films were also performed, as shown in Figure S3a. The oscillation periods of the Au nanocubes in both aqueous solutions and the PVA film were similar and unaffected by the surrounding environments. In our previous study, the breathing mode of assembled metal nanospheres was less affected by the surrounding environment, while the extensional mode of nanorods with a large length-to-radius ratio was sensitive to the viscoelastic environment, in accordance with the assignment of the breathing modes in the present Au nanocubes. Therefore, both acoustic vibrations are breathing modes driven by thermal expansion, owing to their similar phases and Qs and less environmentally affected oscillation frequencies.

The vibrational modes were simulated, and the corresponding profiles are illustrated in Figure 2e. The displacements for expansion/shrinkage in the two modes are labeled as I/I’ and II/II’. The maximum and minimum deformations are represented by the reddest and bluest sections, respectively. For the Au nanocubes, the low-frequency mode I due to the breathing mode corresponds to displacements from tip-to-tip. The low-frequency mode for our Au nanocubes shows similar characteristics to the reported experimental and simulation results for large Ag nanocubes. The high-frequency mode II represents a breathing mode with large displacements in the face-to-face and edge-to-edge directions, similar to the overtone breathing mode of Ag nanocubes with the main displacement only in face-to-face direction. In the TA measurements of metal nanoparticles, the detected vibrational modes resulted from the coupling effect of phonon and plasmon modes. The low-frequency mode could be detected due to the high sensitivity of the plasmon bands to the tips of the nanocubes. The coupling of phonon and plasmon modes became the strongest when the regions of the strongest EM field (plasmon mode) and the largest displacement (phonon mode) overlapped. The high-frequency mode was assigned to the breathing mode of the whole nanocube. Similar to Au nanospheres, the breathing mode induced a plasmonic shift, mainly due to photoelastic coupling. The spectral shifts induced by the two modes are plotted in the upper panel of Figure 2c. The amplitude of the spectral shift for mode I is smaller than that of the high-frequency mode II, as shown by the results in Table 1, in good agreement with the amplitudes of each mode by FFT, as shown in Figure 2d. In the reported simulation results, reverse spectral shifts were observed for two vibrational modes induced by size expansion of Ag nanocubes. Hence, the two vibrational modes in our Au nanocubes represented similar spectral shifts (similar phases) to the expansion in mode I combined with the shrinkage in mode II, as illustrated in Figure 2e.

Variation in the Au nanopolyhedron geometries allowed controlling the coherent acoustic vibrational modes. TA measurements were performed with 400 nm laser excitation for Au octahedron and nanocuboctahedron. Besides multivibrational modes, a phonon beating pattern was clearly distinguished in Au nanocuboctahedron. The coherent acoustic phonon modes were analyzed by the modulated portion of the oscillation dynamics of the bleach peak wavelengths, as shown in Figure 3a,d. For both Au nanostructures, two frequency components were distinguished by FFT, as illustrated in Figure 3b,e. The oscillation dynamics in Figure 3a,d were fitted with eq 1. The results are listed in Table 1, and the two damped oscillation components are plotted in the upper panels of Figure 3a.d. Similar vibrational frequencies (51.4 and 57.8 GHz) and similar amplitudes of the two modes in the Au nanocuboctahedrons resulted in the phonon beating pattern, which has also been reported for triangular-shaped Al nanocrystals. As shown in Table 1, the phases and Qs of the low and high frequency modes displayed small differences within the Au nano-octahedrons and within the nanocuboctahedrons, which suggested the same driving mechanism of thermal expansion. Similarly, the vibrational frequencies in the Au nano-octahedrons and nanocuboctahedrons are less affected by surrounding environments, as shown in Figure S3b and S3c. The displacements of their corresponding vibrational modes were simulated by FEM and are presented in Figure 3c.f. In both Au nano-octahedrons and nanocuboctahedrons, the low frequency vibrational modes are tip-to-tip breathing modes (1/1’), similar to those of the Au nanocubes. For the high
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Histograms of the size distributions of Au nanopolyhedrons, steady-state and oscillation dynamics of bleach peak wavelengths of Au nanopolyhedrons in aqueous solutions and PVA films (PDF)

**CONCLUSIONS**

In this study, we examined the ultrafast dynamics of coherent acoustic phonon vibrations in Au nanopolyhedrons, including nanocubes, nano-octahedrons, and nanocuboctahedrons, by TA spectroscopy. Within each nanoparticle, two acoustic vibrational modes were detected. Both were assigned to the breathing mode due to being less affected by surrounding environments and their similar phases and Qs, and hence were triggered by the same mechanism, thermal expansion. The low-frequency mode corresponded to the acoustic oscillation in the tip-to-tip direction. The high-frequency mode was affected by the surface morphology and represented edge-to-edge displacement in Au nano-octahedrons, face-to-face displacement in Au nanocuboctahedrons, and a combination of edge-to-edge and face-to-face displacements in Au nanocubes. The detected vibrational modes are coupled sensitively with their plasmon modes. In addition, a coherent phonon beat was observed in Au nanocuboctahedrons, in which the two breathing modes represented similar frequencies. Our results provide the possibility to control optomechanical properties by metal nanostructure morphology engineering.

**EXPERIMENTAL METHODS**

Au nanopolyhedrons with well-defined sizes and shapes were synthesized by a seed-mediated literature method.\(^\text{10}\) The samples in PVA films were prepared on glass plates by a drop-casting method\(^\text{16}\).

Steady-state absorption spectra were measured using a U4100 spectrophotometer (Hitachi). TA spectra were measured by a conventional pump-probe method.\(^\text{27}\) The pump beam was the second harmonic of an amplified Ti:sapphire laser (Spectra Physics, 1 kHz, 60 fs, 800 nm). The probe beam, a supercontinuum generated by the excitation of D\(_2\)O with a fundamental laser, was focused on the samples and detected using a CCD detector (Princeton Instruments, Spec-10-100LN). A mechanical delay stage in the probe light path was used to change the time difference between the pump and probe beams. Subsequently, the time-resolved difference absorption at a certain delay time after excitation was calculated by the logarithm of the intensity ratio of the probe light as the pump light fluctuated on and off by the chopper moving between the open and closed positions. Numerical simulations were conducted using finite element analysis (COMSOL Multiphysics 5.4, Structural Mechanics Module) to correlate the experimental data with the acoustic modes of Au nanopolyhedrons. The eigenfrequency analysis was performed using the equation of motion. The shapes and sizes of the samples were determined by the experimental results from TEM and SEM measurements. The mesh of each structure was a finer physics-controlled mesh. The mechanical properties of Au were defined according to the bulk values (Young’s modulus = 79 GPa, Poisson’s ratio = 0.42, and density = 19 300 kg/m\(^3\), respectively).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05806.

Histograms of the size distributions of Au nanopolyhedrons, steady-state and oscillation dynamics of bleach peak wavelengths of Au nanopolyhedrons in aqueous solutions and PVA films (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Li Wang – Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337, Japan; orcid.org/0000-0003-3024-5925; Email: wangli@kwansei.ac.jp

Naoto Tamai – Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337, Japan; orcid.org/0000-0002-7343-6564; Email: tamai@kwansei.ac.jp
Authors
Shohei Takeda — Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337, Japan
Kyota Sato — Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
Masanori Sakamoto — Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
Toshiharu Teranishi — Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan; orcid.org/0000-0001-5018-8590

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05806

Notes
The authors declare no competing financial interest.

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