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Coherent phonon vibration of periodical gold nanocuboids by near IR transient absorption spectroscopy

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Introduction Surface plasmon resonance (SPR) of metal nanostructures has attracted keen interest due to the potential applications in surface-enhanced Raman scattering, optical biosensing, imaging techniques, etc. The shift of SPR frequency in the assembled nanostructures was shown to have a exponential relationship with the ratio of particle size and interparticle separation. However, it is not so clear whether the frequency of the coherent phonon vibration obeys the universal scaling behavior similar to SPR frequency or not for different geometry of metal nanostructures from nanodisks, for example, nanocuboids.

Experiments The periodic gold nanocuboids were fabricated on quartz slides by electron beam lithography. The typical AFM images of periodic gold nanocuboids were shown in Fig. 1 with the size of 150×150×15 nm^3 for each cuboid. The central distance between two single nanocuboids was about 780 nm as shown in Fig. 1(a). Two nanocuboids called the pair in Fig. 1(b) were adjacent in the direction of their diagonal lines with the gap of 9 nm between two vertexes and the central distance between two pairs was about 700 nm. To investigate the relationship between coherent phonon vibration and gaps, other two types of periodic systems of pairs with various gaps of 0, 1.8, 3.5, 5.3, 7.1, 8.8 and 10.6 nm were also prepared, in which the separation between the sides of two pairs were 100 and 300 nm, respectively, and symbolized by D100 and D300. Transient absorption spectra were measured by pump-probe method with polarized 400 nm excitation and near IR probe laser pulses.

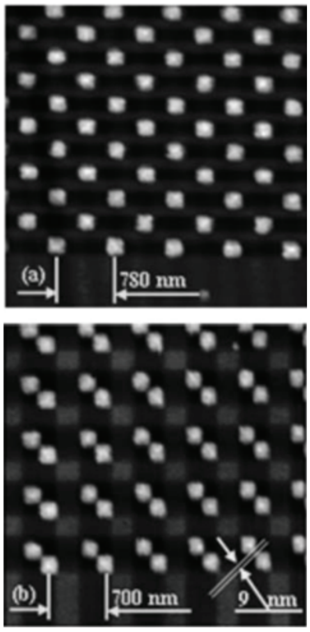

Fig. 1. AFM images for the single (a) and pair (b) of gold nanocuboids.

Results and discussion Fig. 2(a) illustrates the SPR spectra of the single and the pair with the polarization of -45° and +45° to the perpendicular, respectively, examined by a probe pulse of white-light continuum. The peaks by fitting a Lorentzian to the spectra were 920 nm for the single irrespective of the polarization and shifted from 953 nm to 997 nm for the pair corresponding to the probe polarization of -45° and +45°. The shift of bleach peaks obtained from the transient absorption spectra were plotted in Fig. 2(b) for the single and the pair with different polarization and fitted by a exponential decay plus a damped cosine function. The similar oscillation periods (77 ± 1 ps) induced by coherent phonon vibration were observed for both nanocuboids while the damping of the pair was faster than that of the single, which may be attributed to local environmental difference and also polydispersity of the samples. Moreover, SPR bands for the pairs of D100 and D300 were red-shifted with the decrease of the gaps while the shift tendencies for both were difference. The oscillation of the coherent phonon for D100 and D300 were observed and fitted by several frequency components according to the Fourier spectrum. Those higher acoustic vibration modes will be discussed by the theoretical calculation related with the asymmetries of the samples.

Two simplified vibrational modes were used in the simulation by the finite-difference time-domain (FDTD) method to estimate the relative change of the size of the single nanocuboid as shown in Fig. 3. Model 1, quasi-extensional mode, with constant volume and variable aspect ratio shows the oscillation of one side length is ~1.5 nm, about ±1% of the original length 150 nm, while model 2, quasi-breathing mode, with variable volume and constant aspect ratio presents the oscillation of one side length is ~5 nm (±3%).

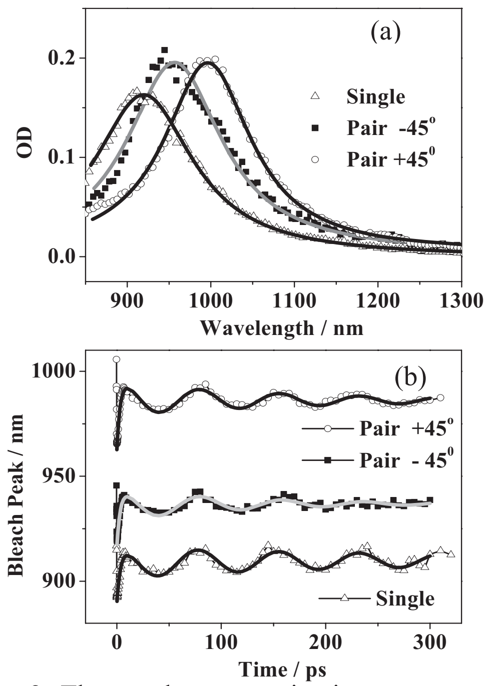

Fig. 2. The steady-state extinction spectra of the single and the pair with the polarization of -45° and +45° to the perpendicular, respectively (a) ; the corresponding shift of the bleaching peaks for the single and pair with two polarization (b). +45° means the direction of the long diagonal line of the pair as one unit.

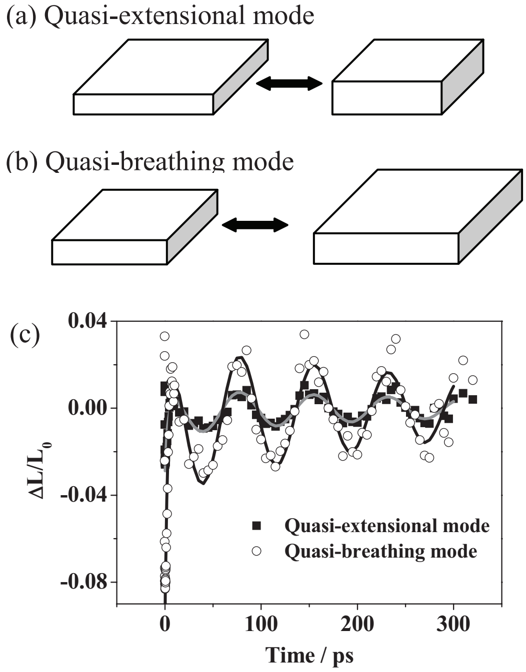

Fig. 3 The schematic diagrams of model 1, quasi-extensional mode with constant volume and variable aspect ratio (a); and model 2, quasi-breathing mode with variable volume and constant aspect ratio (b); side length change ($\Delta L/L_0$) as a function of time for two modes in the single nanocuboid array calculated by FDTD method (c).