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Coherent acoustic phonon dynamics of gold nanorods and their environmental effects by transient absorption spectroscopy

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[Introduction] Metal nanoparticles have attracted much interest due to the unique properties of surface plasmon resonance and surface enhanced electric field. With the light irradiation, the relaxation of excited plasmon modes follows the processes of electron-electron scattering, electron-phonon coupling and coherent acoustic phonon vibration combined with heat dissipation to the surroundings. A frequency range from 1 GHz to 1 THz of acoustic phonon vibration have been observed for small sized metal nanoparticles. This kind of mechanical property of metal nanostructures can be applied in ultrasensitive mass sensors and ultrafast sound sources. In this report, ultrafast dynamics of gold nanorods (Au NRs) and nanospheres (Au NSs) dispersed in poly(vinyl alcohol) (PVA) films were investigated at various temperatures. Extensional mode of coherent acoustic phonon vibration for Au NRs and breathing mode for Au NSs were observed. The effects of environments on coherent acoustic phonon vibration for Au NRs were discussed in terms of the mechanical interaction of the polymer matrix and the liquid-solid coupling of the solution.

[Experiments] Five kinds of Au NRs were gifted from Dai-Nippon-Toryo Co., Ltd and four kinds of Au NSs were commercially purchased from Aldrich. Concentrated Au NRs (or NSs) in aqueous solution was dispersed in 2 wt% PVA solutions and spin-casted on glass slides, which left various molar ratios of Au NR to PVA (1 to 400~40,000). Transient absorption (TA) spectroscopy was performed with a conventional pump-probe method described previously. [1]

[Results and Discussion] A representative TEM image of Au NRs is shown in Fig. 1a. The width and length of Au NRs are around 9 nm and 46 nm by fitting the histograms for over 100 nanorods with Lognormal distribution functions. The extinction spectra of Au NRs with 46-nm length in PVA matrix and aqueous solutions are shown in Fig. 1(b). Both transverse- and longitudinal- surface plasmon modes for Au NRs in PVA matrix are red-shifted as compared with those for Au NR solutions due to the

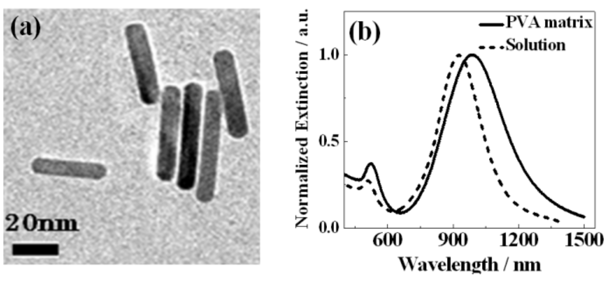

Fig. 1 A TEM image of Au NRs with 9-nm width and 46-nm length (a) and normalized extinction spectra of NRs embedded in PVA matrix and dispersed in aqueous solution (b).

difference of the refractive index between PVA matrix (n = 1.53) and aqueous solution (n = 1.33).

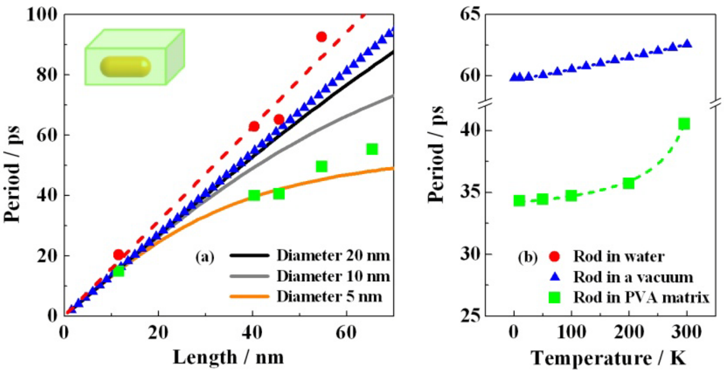

Fig. 2 Experimental periods of coherent phonon vibration of Au NRs in PVA matrix (square), in water (circle) and in vacuum (triangle) were plotted as a function of Au NR length (a). The simulated periods based on pile-soil interaction model are plotted by the solid lines corresponding to 20, 10 and 5 nm diameter of Au NRs. Oscillation periods of Au NRs in PVA matrix (46-nm length) and calculated periods by using Young's modulus $E_{[100]}$ of bulk Au were plotted as a function of temperature (b).

Time dependences of bleaching peak wavelengths can be obtained by roughly fitting some of Gauss functions to TA spectra of Au NR and NS samples. The period of coherent acoustic phonon vibration was estimated by fitting a damped cosine function to the decay profile of bleaching peaks. The oscillation periods of Au NRs in PVA matrices become smaller than the calculations while those of Au NRs in aqueous solution present a bit larger values in Fig. 2a. It is very clear that the oscillation periods of Au NRs are shifted with the surrounding environments. The environmental effects on coherent acoustic phonon vibration for Au NRs were discussed in terms of the mechanical interaction of the polymer matrix and the liquid-solid coupling of the solution.[2,3] A simplified model of pile-soil interaction was introduced for Au NRs in PVA matrix. By considering of the elastic and viscous properties of PVA matrix, the oscillation period of Au NR was found to be affected by their mechanical interaction. The calculated periods were in good agreement with the experimental data as shown by the solid lines in Fig. 2a.

In Fig. 2b, the oscillation periods of Au NRs were experimentally 15 % decreasing from 40.5 ps to 34.3 ps with the decrease of temperature from 294 K to 10 K, while the period of extensional mode for a 46-nm rod was only 4 % decreased by using the elastic property of bulk Au with [100] growth direction. The elastic property of PVA is also changed with the temperature. Therefore, the contribution from PVA matrix should be considered for the temperature effect on the periods of Au NRs.

[References]

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