Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Breathing mode vibrations and elastic properties of single-crystal and penta-twinned gold nanorods

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Dispersion relation for the fundamental extensional mode of penta-twinned gold nanorods

We consider the penta-twinned gold nanorods with the width of W = 15.09 nm and the aspect ratio from 2 to 4 as examples, to examine the validity of the dispersion relation by the long-wavelength limit for the fundamental extensional periods of the penta-twinned gold nanorods. The fundamental extensional periods of those nanorods are calculated by the FE method. The FE models of penta-twinned gold nanorods are constructed with five single-crystal triangular prisms stacked together along a common axis, as illustrated in Fig. 1a. The density and elastic constants used here are the same as those for the FE analysis of breathing modes of twinned nanorods (see the main text). Figure S1 compares the FE-calculated T_{ext} for the considered nanorods with those by the dispersion relation based on the long-wavelength limit. The numerical results agree well with the analytical solutions for the aspect ratio down to 2.5 (within 2%). Thus, the fundamental extensional mode of twinned gold nanorods with an aspect ratio as small as 2.5 could be described by the dispersion relation based on the long-wavelength limit.

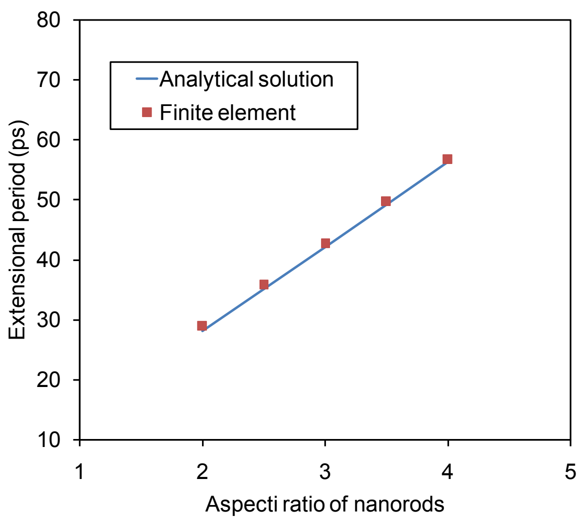

Fig. S1 Comparisons of the fundamental extensional periods of penta-twinned gold nanorods obtained by the FE calculations and the dispersion relation based on the long-wavelength limit. The studied twinned nanorods have a width of 15.09 nm and the varying aspec ratios from 2 to 4.

Damping times for the vibrational motions of gold nanorods

To find the damping times for the extensional and breathing vibrations of gold nanorods, we computed the pressure-related quantity $P = \left(P_{xx} + P_{yy} + P_{zz}\right)/3$ and fitted P to a sum of damping cosine functions

$$P = a + \sum_{i}^{m} b_i \exp\left(-\frac{t}{\tau_i}\right)\cos\left(\frac{2\pi}{T_i}t + d_i\right) \tag{S1}$$

where a characterizes the initial P, b is the amplitude of P for the vibration modes, t is time, τ , T and d are the damping time, period and phase of the vibration modes, respectively, and m is the number of the damped cosine functions. The single-crystal nanorods have one breathing mode while two different breathing modes are observed for the penta-twinned nanorods. Therefore, during the fitting process, we set m = 2 and 3 for the single-crystal and twinned gold nanorods, respectively. Figure S2 illustrates the simulated transient P and the corresponding fits of P to Eq. (S1) for nanorods S1, S3, T1 and T3, in which the transient P at the time 20 ps after the laser irradiation is used for the fitting. Tables S1 and S2 give the fitted damping times for nanords S1-S5 and T1-T6.

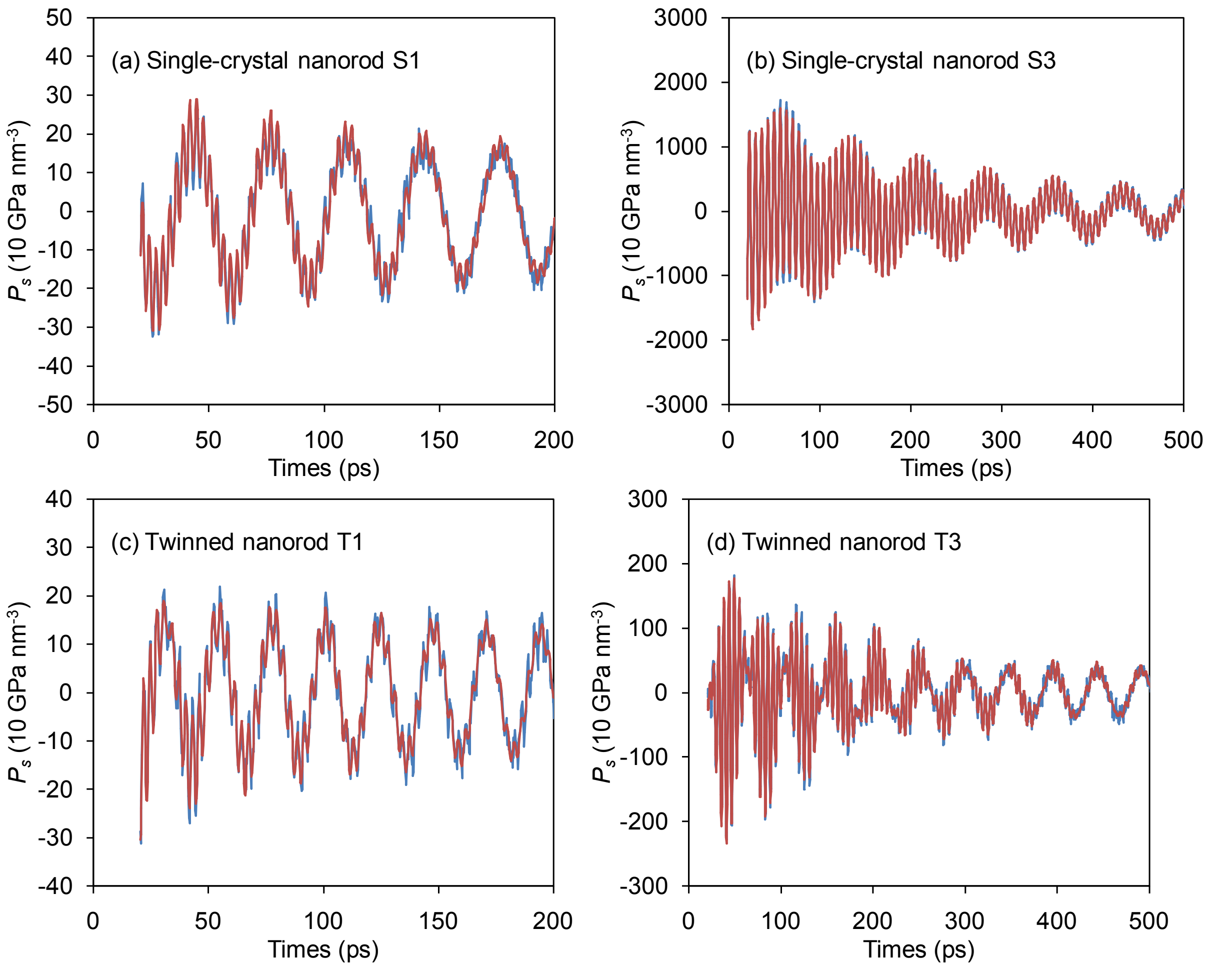

Fig. S2 Fits of the simulated transient $P = (P_{xx} + P_{yy} + P_{zz})/3$ to Eq. (S1) for (a) sample S1, (b) Sample S3, (c) Sample T1, and (d) Sample T3. The blue curves represent the data of *P* by the combined TTM-MD simulations, and the red lines are the fits.

Table S1 Damping times for single-crystal gold nanorods S1-S5 (ps).

Sample #	Extensional mode	Breathing mode
S1	690.17	106.42
S2	1332.39	150.56
S3	2334.75	193.66
S4	3392.59	223.14
S5	3470.23	331.41

Table S2 Damping times for penta-twinned gold nanorods T1-T6 (ps).

Sample #	Extensional mode	Breathing mode	
		Vertex motion	Edge motion
T1	849.06	121.96	26.77
T2	1675.07	118.05	109.22
T3	2551.61	146.37	145.00
T4	4789.28	243.99	226.35
T5	5316.99	239.26	270.68
T6	3035.19	266.52	325.39