Supplemental Information for:

On the Measurement of Relaxation Times of Acoustic Vibrations in Metal Nanowires

Tuphan Devkota,[a] Debadi Chakraborty,[b] Kuai Yu,[c] Gary Beane,[a] John Sader[b] and Gregory V. Hartland[a,1]

[a] *Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States*

[b] *ARC Centre of Excellence in Exciton Science, School of Mathematics and Statistics, The University of Melbourne, Victoria 3010, Australia*

[c] *College of Electronic Science and Technology, Shenzhen University, Shenzhen, 518060, P. R. China*

[1] Corresponding author. e-mail: ghartlan@nd.edu; telephone (574) 631-9320

Calculation of Vibrational Frequencies and Quality factors:

The quality factors and vibrational frequencies for the nanowires were calculated using both finite element simulations (COMSOL Multiphysics), and the standard analytic expression for the breathing modes of a circular cylinder.[1, 2] The analytic expression is obtained by solving the equations for radial displacement and stress of an isotropic cylinder in a homogeneous environment.[1, 2] Assuming that the displacements for the cylinder ($i = c$) and medium ($i = m$) are given by Bessel and Hankel functions of the first kind, and that there is continuity of radial stress and strain at the cylinder-matrix interface, the solution yields the eigenfrequency equation

$$\rho_c\left[c_{L,c}^2 k_c R\frac{J_0(k_c R)}{J_1(k_c R)} - 2c_{T,c}^2\right] = \rho_m\left[c_{L,m}^2 k_m R\frac{H_0(k_m R)}{H_1(k_m R)} - 2c_{T,m}^2\right] \quad \text{(S1)}$$

where $k_i = \omega/c_{L,i}$, ρ_i, $c_{L,i}$ and $c_{T,i}$ are the wavevector, density and longitudinal and transverse speeds of sound in medium i. Numerical solution of Equation (S1) yields a series of complex eigenfrequencies, with frequencies and damping rates of $f = Re[\omega]/2\pi$ and $\gamma = Im[\omega]$, respectively. The quality factor is defined as $Q = \pi f/\gamma = Re[\omega]/2Im[\omega]$. Note that Equation (S1) does not include effects from solvent viscosity.

The damping of the vibrational motion that comes out of this analysis is purely from radiation of sound waves from the nanowire into the medium. Calculations of the breathing mode frequencies and quality factors using the theory developed in Ref. [3] that explicitly take into account the viscoelastic properties of the medium give identical results to those from Equation (S1). Equation (S1) gives an explicit relationship between size of the nanowire and the breathing mode frequency, which can be used to determine the dimensions of the nanowires in the experiments. For example, for water we obtain $k_{Au}R = 2.280 + 0.026i$ for the fundamental

breathing mode, which yields a vibrational frequency and quality factor of $f = 2.280 c_{L,Au}/2\pi R$ and $Q = 2.280/(2 \times 0.026) = 43.8$, respectively.

Finite element simulations for a nanowire on a solid surface where performed through a two-dimensional Eigenfrequency calculation in the Solid Mechanics Physics Module of COMSOL. In these calculations a pentagonal gold nanowire was placed on top of a glass slab. The dimensions of the slab were much larger than the wire diameter (in general, greater than 20 times in any direction), and the corners of the pentagon were rounded slightly. Free boundary conditions were used on the top and bottom of the structure, and periodic boundary conditions were used at the edges.

Placing the nanowire in contact with the slab hybridizes the breathing modes of the nanowire with vibrational modes of the slab. The hybridized modes that involve the breathing motion were identified by projecting the normal modes determined by COMSOL onto the volume change of the nanowire. In our two-dimensional calculations this is done through the normalized surface integral

$$\frac{\iint (u \cdot x + v \cdot y) dS}{\sqrt{\iint (u^2 + v^2) dS} \sqrt{\iint (x^2 + y^2) dS}} \tag{S2}$$

where (u,v) and (x,y) are the displacements of the normal mode and the expansion of the nanowire, respectively, and the integral is performed over the area of the nanowire.[1, 4] The results from this calculation are plotted against the frequencies of the normal mode in the main text. The vibrational quality factors were determined by simply fitting the amplitude versus frequency data to a double Lorentzian function $F(\nu) = \sum_i A_i \gamma_i / \left\{ (\nu - f_i)^2 + (\gamma_i/2)^2 \right\}$, and the quality factor is $Q = f/2\gamma$. Note that changing the dimensions of the slab changes the number of normal modes per frequency interval, but does not strongly affect the vibrational quality factors. This is

shown in Figure S1, where the vibrational spectra are presented for large (top) and small (bottom) glass slabs.

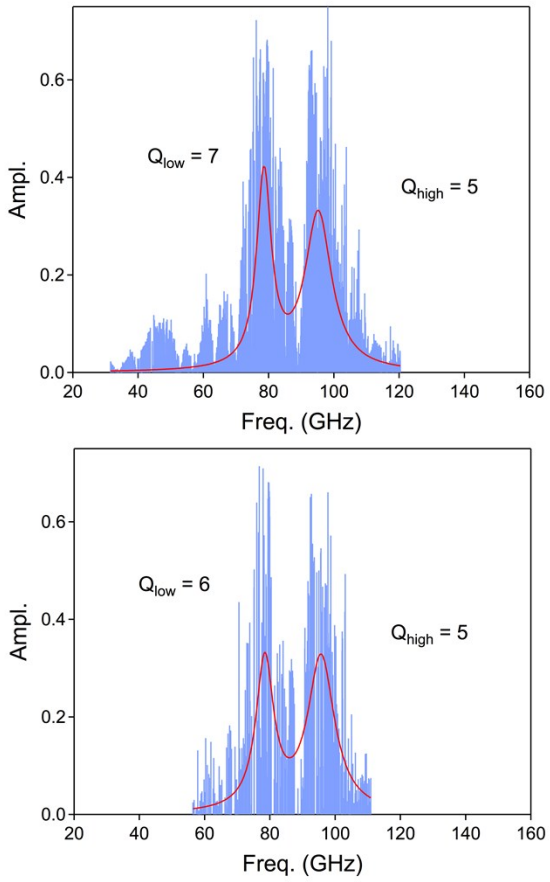

Figure S2: Mode analysis calculations for a 30 nm diameter pentagonal nanowire on a solid glass surface. The dimensions of the glass slab (width x height) were 1200 nm x 600 nm for the top panel, and 600 nm x 300 nm for the bottom panel.

Additional Experimental Data:

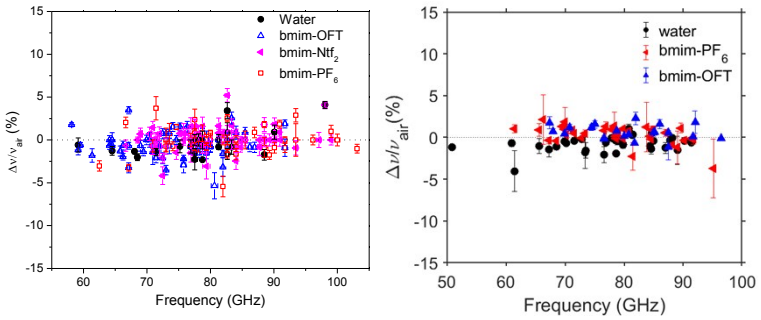

Figure S2: Change in frequency with addition of the liquid for the supported nanowires (left) and suspended nanowires (right) from the nominally 30 nm diameter sample.

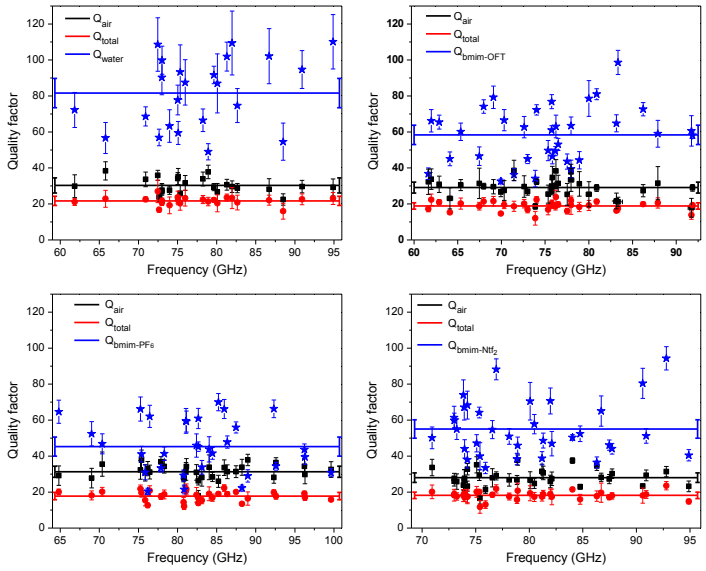

Figure S3: Quality factors for air, total quality factors in the liquid, and quality factors for liquid damping for the supported nanowires from the nominally 30 nm diameter sample.

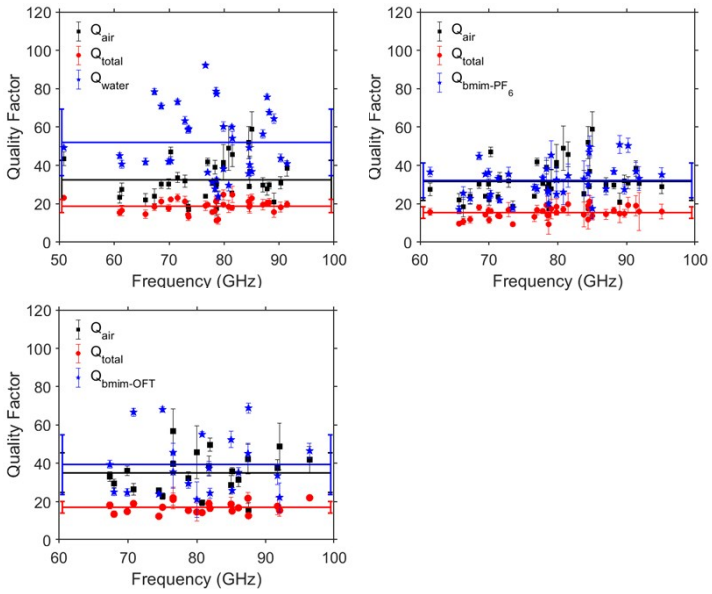

Figure S4: Quality factors for air, total quality factors in the liquid, and quality factors for liquid damping for the suspended nanowires from the nominally 30 nm diameter sample.

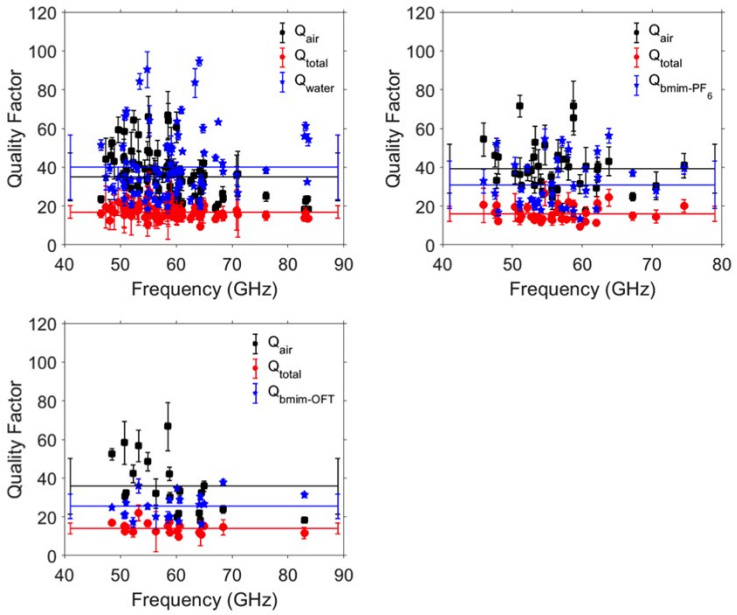

Figure S5: Quality factors for air, total quality factors in the liquid, and quality factors for liquid damping for the suspended nanowires from the nominally 75 nm diameter sample.

References:

1. T. A. Major, A. Crut, B. Gao, S. S. Lo, N. Del Fatti, F. Vallee and G. V. Hartland, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4169-4176.
2. T. A. Major, S. S. Lo, K. Yu and G. V. Hartland, *J. Phys. Chem. Lett.*, 2014, **5**, 866-874.
3. D. Chakraborty, G. V. Hartland, M. Pelton and J. E. Sader, *J. Phys. Chem. C*, 2018, DOI: 10.1021/acs.jpcc.7b09951.
4. A. Crut, V. Juve, D. Mongin, P. Maioli, N. Del Fatti and F. Vallee, *Phys. Rev. B*, 2011, **83**, 205430.