Tuning Nanoelectromechanical Resonators with Mass Migration

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ABSTRACT

We demonstrate tuning of nanoelectromechanical resonators via mass migration. Indium nanoparticles can be reversibly migrated to different locations along cantilevered multiwalled carbon nanotube resonators using electrical currents as the control parameter. Nonvolatile mass redistributions result in stable resonant frequency shifts as large as 20%. The tuning method is robust and can be utilized for nanoelectromechanical resonators operating at frequencies from audio to microwave.

Nanoelectromechanical resonators¹⁻¹⁵ serve as versatile platforms for technologies ranging from mass sensing^{1,4-8} to radio signal reception⁹ to observation of quantum phenomena.¹⁰ Fundamental oscillation frequencies span kilohertz to gigahertz.^{1-4,11} For many applications, tuning of the resonant frequency is highly desirable. Frequency tuning of nanomechanical resonators has been previously achieved by altering the effective length of the resonator,^{9,12} or by tensioning,^{3,7-10,13-15} but each of these methods has significant drawbacks. Length change is an irreversible process for singly clamped resonators⁹ and is possible only with special geometries for doubly clamped resonators.¹² Tensioning methods typically necessitate high dc bias voltages (100-1000 V),^{9,13} and the range of tuning is inherently limited by the system's bearable tension (including tensile strength of clamps).

Mass sensing applications of nanoelectromechanical resonators exploit resonant frequency shifts resulting from direct mass adsorption to the resonator.^{1,4–8} Conversely, controlling the effective mass of a resonator would lead to a new way of tuning its resonant frequency. Here, we demonstrate reversible frequency tuning of multiwalled carbon nanotube (MWNT) resonators by employing mass migration. Indium is controllably transported to different locations on the MWNT resonator by brief application of a dc electrical transport current at small bias (2–3 V). The indium can be transported either on the outer surface of the MWNT or in the hollow region within its core. Mass redistribution along the resonator gives reversible tuning with frequency shifts exceeding 20%.

Figure 1a is a schematic drawing of the experimental configuration. All experiments are performed inside a JEOL



Figure 1. MWNT as a cantilevered nanomechanical resonator. (a) Schematic drawing of a resonance experiment. A multiwalled carbon nanotube (MWNT) serves as a cantilevered nanomechanical resonator. Between the MWNT sample side and the mobile tungsten probe, dc and ac voltage are applied. At a mechanical resonance, the MWNT starts to vibrate, which can be observed with TEM. (b) TEM images of a MWNT when it is off and on the resonance. The driving ac frequency is 17.5 MHz for the resonance. The scale bar is 200 nm.

2010 transmission electron microscope (TEM) operated at 100 keV, equipped with a nanomanipulation platform (Nanofactory Instruments AB). Arc-grown MWNTs are attached to an aluminum wire using conductive epoxy. The wire is then mounted to the stationary side of the holder on the TEM insertion stage. An etched tungsten probe coated with $\sim 20-30$ nm indium via e-beam evaporation is mounted to the opposite mobile side of the holder. When a MWNT candidate for the experiment is identified, the tungsten probe

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is moved so that the distance between the probe and the MWNT is approximately 300 nm. Mechanical resonance of the singly clamped MWNT is then induced by application of an ac electric field between the MWNT and the tungsten probe.

Due to the coupling between the induced charges at the tip of the nanotube and the electric field, an alternating force is applied to the MWNT. If the frequency of the forcing function matches the mechanical resonance frequency of the MWNT, the MWNT physically vibrates with enhanced amplitude,¹⁶ which can be observed visually using the TEM imaging system. Figure 1b shows TEM images for a MWNT driven on and off resonance. In a typical experiment, TEM video is recorded while sweeping the ac frequency. By analysis of the video, the response of the MWNT resonator is determined. For resonators with resonant frequency higher than 20 MHz, a few volts of dc bias (which causes more induced charges at the tip) are usually applied together with the ac drive to enhance the resonant response. For a given MWNT resonator, we use the same dc bias value throughout the experiment to minimize dc-driven resonant frequency shifts via tension effects. However, the dc-dependence of the resonant frequency is very small, typically less than 0.1%/V in our experiments. Resonant frequencies typically lie between 5 and 150 MHz with quality factors of 300-1000.

Since the resonant frequency of the MWNT is a sensitive function of the mass distribution of the resonator, additional mass-loading provides a means to tune, for a given MWNT, the resonant frequency. We accomplish this by migrating indium to different locations on or in the MWNT. TEM images a-d in Figure 2 show a mass migration process onto a MWNT. If the tungsten probe is moved to make contact with the normally free tip of a MWNT, it completes an electrical circuit through the MWNT (Figure 2b). With suitable dc current ($\sim 40 \,\mu A$) flowing from the probe through the MWNT, indium can be transported from the probe, which serves as a reservoir, to nucleate at several locations on the MWNT, as shown in Figure 2c.19,20 Reversed dc currents from MWNT to the probe remove indium particles from the MWNT and return them to the probe. The indium addition process can be repeated for the MWNT after a full addition/ removal cycle. The migration will be discussed later in this Letter.

After a new mass distribution is established along the MWNT, the tungsten probe is retracted to the resonance experiment position (~300 nm gap between the tungsten probe and the MWNT), and a resonance experiment is initiated by sweeping the ac drive frequency. With MWNT cantilevers of different mass distributions, we observe the resonance shifts shown in Figure 2e. As expected, the resonator has lower resonant frequency with increased effective mass, which is the fundamental concept of mass sensing using mechanical resonators. The inset to Figure 2e shows TEM images of a variously mass-loaded MWNT. (i), (ii), and (iii) correspond respectively to the pristine (unloaded) MWNT, after the initial mass loading, and after cleaning and mass reloading. From the initial indium



Figure 2. Indium mass migration and resulting resonant frequency shifts. (a–d) Sequential TEM images of an indium mass migration process onto a MWNT nanomechanical resonator. (a) A MWNT before indium mass migration. (b) Electrical contact between the tungten probe and the MWNT for indium migration. The indium-covered tungsten probe serves as an indium reservoir. (c) Indium mass migration to the MWNT from the tungsten probe via dc current. (d) Repositioning the tungsten probe to the resonance experiment position after mass migration. The scale bar is 100 nm. (e) Resonance response for different indium configurations. The dc bias is 3 V for the response. The inset to Figure 2e shows TEM images of a variously mass-loaded MWNT. (i), (ii), and (iii) correspond to the pristine (unloaded) MWNT, after the initial mass loading, and after cleaning and mass reloading, respectively. The scale bar is 100 nm.

migration process (ii), we obtain a frequency shift larger than 20%.

Of interest is the controllability and repeatability of the mass loading process via the current-driven mass migration onto the MWNT. For the moment we consider these characteristics only for mass loading on the MWNT exterior. On the basis of the observed mass migration rates, we find that it is possible to target a resonant frequency shift as precisely as 1%. Within this precision limit, the system can be repeatably tuned to any desired frequency. An interesting question arises if a given target frequency need always be associated with an identical mass distribution. As an example, we consider (ii) and (iii) in Figure 2e. Although the indium particle nucleation sites are not all exactly the same for (ii) and (iii), the majority of the sites do coincide. Defects such as a Stone-Wales (SW) configurations can lower the indium adsorption energy on the nanotube, which facilitates the indium nucleation at the defects.²⁰ It is plausible that the observed nucleation sites have this preference for nucleation due to such structural defects. The biggest observed difference is that the far right nucleation site at (ii) has disappeared at (iii). The possible reason for this is a Joule-heating-assisted annealing which cures and/or migrates structural defects. The defect sites of the MWNT close to the tungsten probe would be most affected since the Joule heating is biggest at the contact point between the tungsten probe and the MWNT.¹⁹



Figure 3. Encapsulated indium movement and resulting resonant frequency shift. (a) TEM images of an indium inclusion at two different locations in a MWNT. The scale bar is 100 nm. (b) Sequential TEM images of indium movement over a 50 s period while a dc bias is applied through the MWNT. The scale bar is 50 nm. (c) Resonance response for (I) and (II). The dc bias is 10 V for the response.

Maintaining the number of these nucleation sites and their locations leads to precise control of the detailed mass distribution, relevant to higher-order resonances.

For the experiments described above and shown in Figure 2, the indium was migrated to different positions on the outer surface of the MWNT. An alternative approach can be used for mass migration along MWNT resonators. Previous work has shown that a MWNT can serve as a nanopipet, where mass transport occurs through the hollow core of the MWNT.²¹⁻²³ Such a mechanism can also be used to controllably mass load and tune the MWNT resonator. To demonstrate this, we first insert indium into the core of a preformed MWNT. We select a MWNT which has an open free end and then move the tungsten probe so that indium is located at this opening. The indium is then injected into the MWNT core with the application of high currents (\sim 300 μ A). After insertion, the indium can be migrated as a unit and precisely positioned axially within the MWNT core using an applied dc current bias with ~ 1 nm control.

Figure 3a shows TEM images of a MWNT with indium placed at different, preselected core locations. Figure 3b shows sequential TEM images of indium movement over a 50 s period during which a current of $\sim 250 \ \mu$ A is applied through the MWNT. When the direction of current is reversed, the movement of indium is reversed. Changes of the indium location within the MWNT core allow tuning of the resonance frequency. Figure 3c shows resonance frequency responses for the two locations of indium mass as shown in Figure 3a. The observed resonant frequencies are 65.0 and 64.1 MHz. As expected, case (I) with indium closer to the MWNT tip has a lower resonant frequency since the effective indium mass is here greater.

We find that, as for most resonators, the vibrating MWNT has a linear response for low drive amplitude (with driveamplitude-independent resonance frequency and symmetrical response line shape) and for large drive amplitude a nonlinear response (for which the line shape becomes asymmetrical and the resonance frequency becomes a function of drive amplitude). For the experiments described here, we use a drive amplitude large enough for reliable response detection inside the TEM, with response just at the transition between linear and nonlinear behavior. In this regime the resonance frequency is unaltered (within 0.1%) from its intrinsic, linear, value, but slight asymmetries do arise in the line shape, as seen in Figures 2e and 3c. Occasionally, we have seen the onset of multiple resonances (mode splitting), as exemplified by the "hump" structure in response (II) in Figure 3c.²⁴

For a given applied axial MWNT electrical current, the direction of indium movement is different for encapsulated indium than for surface-located indium. This implies that the details of the responsible transport are different. The driving force of conventional electromigration includes a carrier wind force and a direct electrostatic force.^{21,25} The carrier wind force has been suggested to be the dominant force for metals encapsulated within MWNT cores,²¹ while the direct electrostatic force might dominate atom transport for outer-surface-bound indium.^{19,20} Indeed, the direction of indium transport (relative to the applied current) can vary dramatically even in non-nanotube host systems: indium electromigrates in the opposite direction of the electrical current in a sample of bulk indium, while it electromigrates in the same direction of the electrical current when located on a silicon surface.²⁵

To estimate resonant frequency shifts resulting from indium mass migration over the surface and through the cores of MWNTs, we resort to classical Euler–Bernoulli beam theory and the Rayleigh–Ritz theorem.^{26–28} If tensioning is ignored (a good approximation for the experiments here under discussion), the Euler–Bernoulli beam equation is

$$\frac{\partial^2}{\partial x^2} \left(E I \frac{\partial^2 y(x,t)}{\partial x^2} \right) = -\rho A \frac{\partial^2 y(x,t)}{\partial t^2} \tag{1}$$

where $y(x,t) = y(x)e^{-i\omega t}$ is the transverse displacement of the beam along its length, *E* is the Young's modulus, *I* is the areal moment of inertia, ρ is the mass density, and *A* is the cross-sectional area.²⁶ Solving the equation gives the fundamental resonant frequency for the MWNT cantilevered beam

$$f_{\rm o} = 0.56 \sqrt{\frac{EI/L^3}{\rho AL}} = 0.56 \sqrt{\frac{EI/L^3}{m_{\rm cnt}}}$$
 (2)

where m_{cnt} is the mass of the MWNT.

Mass adsorption on the MWNT resonator causes a shift in the resonant frequency, which can be estimated using the Rayleigh–Ritz theorem.^{26–28} If indium masses m_i are adsorbed at locations x_i , the resonant frequency is changed to

$$f' = 0.56 \sqrt{\frac{EI/L^3}{m_{\text{cnt}} + \sum_i w(x_i)m_i}}$$
(3)

with $w(x) = Ly_o^2(x)/f_0^L dxy_o^2(x)$. Here, w(x) is the weighting function, which shows the degree of effectiveness of mass on the resonant frequency, and $y_o(x)$ is the fundamental resonant mode shape for a cantilevered beam. In the case of surface migration, nucleation sites and their corresponding weighting functions are predetermined as x_i and $w(x_i)$, while we can change the distribution of mass m_i . On the other hand, in the case of in-channel mass transport, the mass load m is fixed while we can vary its weighting function w(x). From eqs 2 and 3, we obtain the following relation for the resonant frequency shift ratio²⁸

$$\frac{f'}{f_o} = \sqrt{\frac{1}{1 + \sum_i w(x_i)m_i/m_{\text{cnt}}}} \tag{4}$$

This equation holds only for MWNTs with a uniform radius. If the MWNT has a nonuniform radius and associated nonuniform mass distribution along its length, m_{cnt} is modified to an effective mass, $m^*_{cnt} = \int_0^L \rho A(x)w(x) dx$. We experimentally determine m^*_{cnt} and $\sum_i w(x_i)m_i$ from TEM images and compare the expected resonant frequency shifts with the observed frequency shifts.

Figure 4 shows as a line the expected frequency shift from eq 4, while the dots are the experimental observation values. Red, blue, and other dots are experimental values from Figure 2, Figure 3, and other MWNT resonators, respectively. The experimental frequency shift ratio f'/f_o is obtained from comparison of resonant frequencies without and with mass loading. For the data from Figure 3, the experimental mass unloaded resonant frequency f_o is unknown and estimated frequency 66.2 ± 0.1 MHz is used. We note that the Rayleigh-Ritz theorem can estimate the frequency shifts from mass loading reasonably even when $\sum_i w(x_i) m_i / m_{\text{cnt}}^*$ is substantial. The assumption of the same mode shape $y_o(x)$,^{27,28} which holds only for small $\sum_i w(x_i) m_i / m^*_{cnt}$ values ($\ll 1$), does not restrict the application of Rayleigh-Ritz theorem at least up to $\sum_{i} w(x_i) m_i / m^*_{cnt} \sim 0.8$. Indeed, this method is quite stable to a poor mode shape assumption²⁷ and is expected to be a reasonable way to estimate the resonant frequency for most loaded MWNT resonators. In the case of in-channel mass transport, we calculate that the possible frequency shift range reaches 20% with reasonable dimension assumptions of a MWNT (1 μ m of length with 20 and 10 nm of outer and inner diameters) and a cylindrical-shaped core indium (300 nm length with 10 nm diameters). With the observed controllability of indium position, it is estimated that the resonant frequency can be controlled to a precision of $\sim 0.01\%$.

In summary, we have demonstrated tuning of nanomechanical resonators with mass migration. In situ TEM operations show that indium adsorbed on a MWNT and encapsulated in the hollow channel of a MWNT can be



Figure 4. Resonant frequency shift dependence on the $\sum_i w(x_i)m_i/m^*_{\text{cnt}}$ values. The line is the expected frequency shift from the Rayleigh–Ritz method, eq 4. The dots are the experimental observation values. Red, blue, and other dots are experimental values from Figure 2, Figure 3, and other MWNT resonators, respectively.

transported along the length of MWNT resonators. Either of these methods could also be utilized in a doubly clamped beam geometry,¹¹ where the tuning process is possible without employing a retractable mass-loading probe.

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