Current micro/nanomechanical system are usually based on rigid crystalline semiconductors that normally have high quality factors but lack adaptive responses to variable frequencies—a capability ubiquitous for communications in the biological world, such as bat and whale calls. Here, a soft mechanical resonator based on a freestanding organic–inorganic hybrid plasmonic superlattice nanosheet is demonstrated, which can respond adaptively to either incident light intensity or wavelength. This is achieved because of strong plasmonic coupling in closely packed nanocrystals which can efficiently concentrate and convert photons into heat. The heat causes the polymer matrix to expand, leading to a change in the nanomechanical properties of the plasmonic nanosheet. Notably, the adaptive frequency responses are also reversible and the responsive ranges are fine-tunable by adjusting the constituent nanocrystal building blocks. It is believed that the plasmonic nanosheets may open a new route to design next-generation intelligent bio-mimicking opto-mechanical resonance systems.

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Through millennia of evolutionary advances, plants and animals throughout nature have designed unique mechanisms for locomotion and interaction with the rapidly changing environment. A large basis of these evolutionary mechanisms involve biological components that emit variable frequency signals that are used for deterring predators, sensing, defense and attracting partners for breeding. For instance, bats normally change their outgoing navigation signal for echolocation. Bats can generate variable frequency signals over wideband spectra for ambient flight conditions giving them a wide range of view. After detecting potential prey, this frequency increases over finite distances for precise predation (Figure 1a). Moths use a tympanic membrane where the pretension can be increased by expansion of the ear cavity as a defense mechanism against bats. Dolphins are able to use clicking to generate sonar signals over large spectral ranges for high bandwidth communications. Mammalian cochlea are an efficient source of transforming sound frequencies within the auditory nerve having little power requirements. From these examples prevalent throughout nature, tunable frequency devices are an integral part for communications and bandwidth, sensing the surrounding environment, interaction between complex systems and they also provide great insight into evolutionary adaptations. For animals, these variable frequency mechanisms are relatively quite small in size, have simple tuning mechanism designs and low tuning power requirements. Furthermore, plants, animals and viruses are highly adapted to using sunlight (photothermal) for energy and cellular interaction.

NEMS (nano electromechanical systems) have become a promising technology due to their low mass, high stiffness, and robust behavior. NEMS technology has become more predominant in daily life as manufacturing techniques for the synthesis of nano-scale devices and their systematic integration with electronic components and circuitry has advanced. In particular, their low mass, high stiffness, and quality factor make NEMS well suited as resonating devices in high frequency spectra; this allows NEMS resonators to be widely adopted in many potential science and engineering applications, such as, vibration and optical absorbers, electronics, energy-harvesters, and as biomolecular sensors. Resonator design is based on matching a device’s fundamental frequency with the surrounding environment. However, this leads to an inherent drawback, if the operating frequency of a device does not match the intended use...
or the ambient frequency shifts, then the resonator does not operate; moreover, manufacturing imperfections also alter the intended resonance frequency of a device which can lead to frequency variability. Due to these reasons, adaptive devices are of significant interest because they are frequency tunable due to a controllable external mechanism. Furthermore, when integrating with micro and nano-scale devices, the mechanism for an adaptive response also needs to be considered, as this will affect the size, manufacturing procedure, tunable range, design complexity, cost and feasibility of a proposed design. Compared with other tuning techniques, optical stimulation allows for a non-contact method using an external light source. A major concern for optically tunable devices is the achievable broadband frequency range and the power required to tune the devices. In general, organic optically tuned resonators inhibit large tunability, and the power required to tune the device is high, in contrast, inorganic resonators usually have low tuning power requirements but their tunable range is narrow (Figure 1b).

Herein, we show that low tuning power and high resonance tunability can be simultaneously achieved with our ligand-mediated plasmonic nanosheet resonators (Figure 1b). The nanosheets are fabricated using polystyrene-capped Au@Ag nanocubes in a drying-mediated self-assembly process.

The light absorbed by these nanoparticles is transformed into heat due to the photo-thermal effect. The nanoparticles are embedded in a freestanding super-lattice to enhance the induced optical-thermal-mechanical coupling. This type of hybrid organic–inorganic freestanding nanosheet can be used as a nanoelectromechanical resonator with extremely high stiffness and low mass for high bandwidth sensing and actuating applications. The additional advantage of the proposed device is that it requires a non-contact tuning method that does not require leads, electrodes, or other electrical components integrated within the device, allowing for easier stimulation, high efficiency, and easier manufacturing. Compared with traditional substrate supported nanoparticle assemblies in the literature, the authors use this design to demonstrate two major findings in this work. The first is that by using an organic–inorganic plasmonic nanosheet, a wideband tunable range from 55.2 to 34.1 kHz can be achieved for relatively low light intensities. Moreover, the second major finding of this work is that using a plasmonic nanosheet enables wavelength selective photon sensing and actuation, this behavior is significantly increased under plasmonic resonance conditions. Due to the advanced near field light–matter interaction inside the plasmonic nanosheet, the resonance frequency is adaptive to either incident light intensity or incident wavelength which gives the proposed device a substantially robust and adaptive response. This type of technology can also be combined with low-dimensional materials for future optomechanical devices.

1. Results

Recently, noble metallic nanoparticles have attracted extensive attention due to their extraordinary optical and electrical characteristics; these metallic nanoparticles can enhance light absorption and scattering in materials and devices. However, absorption and subsequent temperature increasing have often been considered as undesirable effects, and most research focuses on the optical properties of metallic nanoparticles. Moreover, it has been demonstrated that plasmonic metallic nanoparticles subjected to optical stimulation are an efficient nano heat-source generating localized heating of particles at the nano-scale. This advanced optical-thermal coupling behavior opens a broad new range of applications, including photo-thermal imaging, cancer targeting, and radiation detection.

The structure adopted in this work utilizes gold nanoparticles encapsulated in silver cubes, which are embedded within a polystyrene matrix and suspended on a silicon substrate as shown in Figure 2a. At the center of the device is a square-shaped freestanding membrane with equal lengths that can vibrate in the out-of-plane direction. More details about the fabrication procedure are shown in Figure S1, and the corresponding Supporting Information. The particles are well aligned inside the polystyrene matrix which act as intermolecular spring linkages. Polystyrene was selected as the matrix because it has strong near field light matter interaction with gold nanoparticle heaters (see Figure S2, Supporting Information). Characterization was carried out with atomic force microscopy (AFM) and transmission electron microscopy (TEM), and the structural parameters of this
Figure 2. Configuration of the hybrid organic–inorganic nanoplasmonic resonator. a) Schematic design of the device structure showing the connection of particles and the center section represents the free standing plasmonic nanosheet membrane that can resonate in the out of plane direction. b) Atomic force microscopy (AFM) image of the nanoplasmonic membrane (scale bar 250 nm). c) Transmission electron microscopy (TEM) image of the nanoplasmonic membrane (scale bar 250 nm).

The nanosheet can be extracted from the obtained high-resolution images (see Figures 2b, c). The nanoparticle diameter is 11 nm, the silver cube has equal lengths of 25 nm, and the plasmonic nanosheet has overall thickness of 40 ± 2 nm (which is the combination of metal particles embedded in the polystyrene matrix).

Upon successful device fabrication, the dynamic response of the nano-resonator in the frequency-domain was conducted using an external piezoelectric excitation system and the experimental system is schematically illustrated in Figure 3a. The dominant resonance peak was observed at approximately 41 kHz and this corresponded to the first fundamental out of plane vibration mode. The experimental frequency-amplitude and frequency-phase curves for a plasmonic nanosheet resonator with side lengths of 300 µm is shown in Figure 3b, subjected to a driving voltage of $V_g = 20$ mV in air. A Lorentzian line fitted as a damped harmonic model yielded a resonance frequency of $f_0 = 41.2$ kHz, and a quality factor value of $Q = 190$. The authors have further characterized the resonance frequency versus $1/L$ for nine different resonators with side lengths ranging from 90 to 300 µm, all resonators were fabricated on a common base. From the fitted red line in Figure 3c, the dependence of the resonance frequency can be extracted as $f_0 \propto 1/L$, which is expected for square shaped membranes. The average value of the pretension $T_0$ was experimentally obtained as 0.074 N m$^{-1}$, deviations from the fitted line are due to random built-in pre-tension generated during the fabrication procedure from the heterogeneous contraction at the air–water interface during the drying-mediated self-assembly process. Another source of this dispersion is due to the variation of non-uniformly distributed nanoparticles within the super-lattice between devices. The standing out of plane 2D map of the fundamental mode was experimentally obtained and is shown in Figure 3d. During the mapping process, the excitation frequency was fixed at the resonance frequency and the interferometer laser gun was controlled by a stage controller for lateral movement with a sub-0.5 µm resolution and a grid was set up in order to obtain the experimental mode shape. Furthermore, COMSOL simulations of the fundamental mode shape are shown in Figure 3e, the simulated natural frequency was 42.8 kHz showing good agreement between the experiment and simulation. Moreover, comparing Figures 3d and 3e, it has been shown that the mapping procedure shows a near similar shape to the simulated mode shape verifying that it is the fundamental mode shape of the resonator.

The resonance frequency of the device is highly sensitive to the internal in-plane tension and this offers the possibility for a tunable resonance frequency. The pre-tension value depends on the fabrication process; however, using the innovative hybrid organic–inorganic configuration proposed in this work, the strong coupling of the light–matter interaction inside the plasmonic nanosheet enables an adaptive response. The frequency-response curves of a plasmonic nanosheet resonator with $L = 250$ µm under different light intensities has been experimentally obtained and shown in Figure 4a. The intensity of the incident light used was 0, 5, 10, and 15 mW cm$^{-2}$ which was measured using a power-meter. For three of the frequency-response curves recorded, there are slight increases and decreases and this is possibly due to interactions with higher modes of the plasmonic resonator. Typically, tuning of the resonator was quite fast using an optical source demonstrating the low power requirements and this was due to the low mass and strong optical-mechanical...
coupling of the device. It was observed when the plasmonic resonator was subjected to a 15 mW cm$^{-2}$ intensity, the resonance frequency exhibited an extremely large downward resonance frequency shift from 55.2 to 34.1 kHz (approximately 40% of the device’s own fundamental frequency). With increasing light intensity, a consistent down-shift of the device’s fundamental frequency was observed and was due to the polystyrene molecular interlinks axially compressing within the freestanding plasmonic super-lattice due to the hybrid organic–inorganic nature as shown in Figure 4b. This phenomenon was caused by the strong optical-thermal interaction of the plasmonic nanosheet and subsequently this caused the resonance frequency to decrease with increasing light intensity; this behavior was also enhanced as the 2D super-lattice is single-particle thick (40 ± 2 nm) and its resonance frequency is dominated by the in-plane tension of the membrane. During the interaction with an optical source, the electric field strongly drives mobile carriers inside the nanoparticles, and subsequently, the energy gained by

Figure 3. Mechanical vibration mode characterization of the plasmonic super-lattice resonator. a) Schematic representation of the experiment. b) Amplitude/phase-frequency response spectra of one plasmonic nanosheet resonator ($L = 300 \mu m$). c) Measured resonance frequency for several different sized plasmonic membrane resonators as a function of the side length $L$. d) Experimentally obtained fundamental mode shape (at 41.2 kHz). e) COMSOL simulation of the fundamental mode shape (42.8 kHz).
the carriers turn into heat through electron–phonon interaction. Afterward, the generated heat in the nanoparticles diffuses into the polystyrene leading to an elevated temperature.\cite{50,51} The temperature increase caused by the photo-thermal effect consequently drives internal compression (mechanical softening), shifting the resonance frequency downward. The authors have demonstrated the optically adaptive response of the hybrid organic–inorganic plasmonic nanosheet has both high tunability and low tuning power requirements. To further verify the added advantages of the organic–inorganic design proposed in this work, controlled experiments for the frequency-shift properties between a plasmonic super-lattice nanosheet and a Si$_3$N$_4$ membrane resonator (which is a conventional nano-resonator in the literature) with the same side lengths were performed, and the experimentally obtained results are shown in Figure 4c. It was observed that the resonance frequency of the Si$_3$N$_4$ membrane resonator remains constant regardless of the incident light intensity. In contrast, using the plasmonic nanosheet in this
work, the nanoparticles absorb the optical energy and react with the light and this drives a temperature differential in the polystyrene, leading to axial in-plane compression of the polystyrene molecular links. Since the resonance frequency of the super-lattice membrane is dependent upon the internal in-plane tension, a shift in the devices temperature will lead to optically adaptive frequencies.\cite{52} 2D COMSOL simulations of the electric field, temperature distribution, and stress around a single gold-silver nanocube particle are shown in Figure 4d,e, and f, respectively (the nanoparticle diameter is 11 nm and the silver cube has equal lengths of 25 nm). It can be seen that the electric field and temperature distribution is uniform with the wave moving equally outwards in both directions; however, for the stress distribution, the polystyrene develops large internal stress from the photothermal excitation particularly around the points of each nanocube and in turn this can change the intrinsic in-plane tension of the plasmonic nanosheet. The advantages of the photothermal excitation are that there are no physical contacts (i.e., electrodes or wiring), high temperature differentials, high efficiency, and stability for low irradiation (i.e., reversibility). Detailed modelling of the nanoparticle heating effect, shifting the resonance frequency of the device and the temperature frequency shift are given in the Supporting Information. For the device in this work, it was found that large exposure of light for significant periods of time can cause color changes in the plasmonic superlattice; however, if the irradiation is low the resonator cools back down to its initial temperature and has the same resonance frequency.

Plasmonic structures increase internal heat generation, have low absorption, and scatter light over wide frequency ranges, these key attributes allow plasmonic structures to be used for spectroscopy and enhancing solar cell efficiency.\cite{53,54} In this work, the authors demonstrate selective photon sensing using the plasmonic effect, the heating effect becomes especially strong under plasmonic resonance conditions. When the energy of the incident photons is close to the plasmonic resonance frequency of the nanoparticles, the internal heat generation is larger and this is highly dependent upon the morphology of the metallic nanoparticles. According to the measured extinction spectra in Figure 5a, the plasmonic resonance frequency of the super-lattice nanosheet is ideally located in the visible and near-ultraviolet regions (which is around 490 nm). The resonance frequency shift strongly depends on the wavelength of the incident light, this means that incident light of relatively weak intensity can tune the resonance frequency easily, in contrast, using higher wavelengths of light requires more power for tuning. The main reason for this behavior is due to strong optical absorption within the vicinity of the plasmonic resonance. The frequency-shift behavior of a plasmonic nanosheet resonator using two different incident light wavelengths at various light intensities has also been experimentally investigated and is shown in Figure 5b. It was observed that when using a wavelength of 500 nm (close to the plasmonic resonance), the fundamental frequency shifted downward 1456 Hz when subjected to a 2 mW cm$^{-2}$ light intensity. However, using the same light intensity and changing the incident wavelength to 750 nm, a 700 Hz downshift was observed. Therefore, the optically adaptive behavior of the device presented in this work can be selectively tuned using either the incident light intensity or incident wavelength allowing for greater operational flexibility in practical applications. The strong optical-thermal-mechanical coupling in this work enables adaptive tuning of the device using low optical power and is well suited for the micro and nano domains. Having dual conditions for wideband behavior allows for greater control of sensors and actuators with ultra-high sensitivity, which makes this type of resonator well suited for telecommunications, circuits, and precision instrumentation.

### 2. Conclusion and Outlook

In conclusion, self-assembled 2D plasmonic nanosheet resonators with optically adaptive wideband resonance frequencies have been demonstrated. This hybrid organic–inorganic resonator is a new type of broadband nanomechanical system integrating plasmonic, photothermal, and mechanical properties into a nanometer-thick free-standing nanosheet. The
mechanical response of the resonators with and without incident light was experimentally investigated and it was observed that the plasmonic effect down-shifted the resonance frequency of a device and enabled an optically adaptive frequency tunability over 21 kHz with very low incident light intensities. The adaptive photothermal mechanical resonating effect demonstrated in conjunction with the extremely low mass, and large surface area of the nanosheets makes our wideband tunable plasmonic nanosheet resonator well-suited for high bandwidth applications. In addition, their frequency-shift tuning properties show that our soft resonator device could be used for selective photon sensing and actuating applications. The above attributes indicate that our soft plasmonic nanosheet resonators may enable the design of future intelligent bio-mimetic adaptive nanophotonics and nanomechanics.

3. Experimental Section

Fabrication of the Free-Standing Plasmonic Nanosheet: The freestanding plasmonic nanosheet was self-fabricated using a drying mediated technique and was deposited onto a silicon substrate with square holes, resulting in the formation of a freestanding plasmonic resonator. The silicon substrate with square holes was fabricated by micro-machining processes, including silicon nitride thin film deposition, lithography, nitride plasma etching, silicon KOH etching, etc. The square shaped resonator has equal length and has a single particle thickness in the out of plane direction of approximately 40 nm. The plasmonic nanosheet resonator is considered to be fully clamped around the square shaped holes and resonates in the out of plane direction as confirmed through experiments and simulations (see Figure 3d,e).

Mechanical Resonance Frequency Characterization: A piezoelectric plate was mounted on the backside of the silicon die for actuation, and the vibration of the membrane was detected with an optical interferometer and lock-in amplifier. The input signal to the piezoelectric actuation system was controlled via a signal generator.

Simulations: Simulations for the resonance frequency of the plasmonic nanosheet resonator were conducted using COMSOL Multiphysics 5.1. The membrane module was selected for the interface physics to account for the in-plane tension dominated natural frequency of the plasmonic resonator. Table S1, Supporting Information, was used for the input parameters for the simulations. A mesh of 5856 elements using a triangular distribution was used and the eigenfrequency physics solver was used for determining the resonance frequency of the square shaped plasmonic nanosheet resonator. For the 2D simulation in Figure 4, the electromagnetics and heat transfer in solids physics modules were used. A 0.001 convergence criterion was used for all simulations in this manuscript.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

light–matter interaction, optically adaptive materials, organic–inorganic materials, plasmonic nanosheets, tunable resonance frequency

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