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Mechanochemically Controlled Functionalization of Graphene Microdrums

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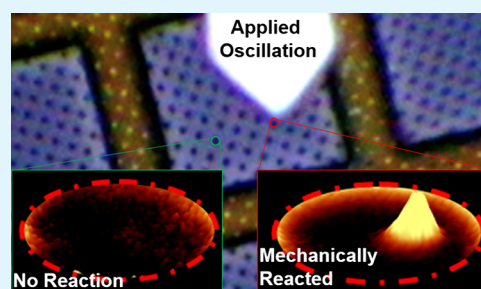
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Supporting Information

ABSTRACT: Mechanochemical reactions involve the use of applied mechanical distortions to reactants to drive chemical reactions. In this work, we demonstrate the use of mechanical force to direct location-specific reactions on suspended bilayer graphene microdrums, by manipulating their geometric landscape, through the introduction of standing-wave oscillations using an atomic force microscope (AFM) probe. By introducing these oscillations into the suspended membrane while it is held in contact with an underlying reactant medium (e.g. water), the mechanically induced oxidation of graphene is observed, whereby the greatest reactivity is seen to occur at the peaks of the induced standing waves, which correspond to the regions of highest local strain in the graphene bilayers. Mapping these reactive regions using Raman microspectroscopy reveals that the radial position of the highest regions of reactivity depends on the applied oscillation frequency, beginning at the center of the microdrums at low frequencies (ca. 1–20 kHz), and then expanding outward at frequencies above 100 kHz. From finite element modeling (FEM) of the frequency-dependent mechanics of the membranes, this change is shown to be consistent with the radial redistribution of the regions of the highest local curvature of the graphene. The ability to use mechanical distortions to drive location-specific functionalization of 2D materials such as graphene provides a new route to the design of nanoscale devices and site-directed catalysis on such materials.

KEYWORDS: 2D materials, site-specific reactivity, finite element modeling, acoustic actuation



INTRODUCTION

Graphene is a two-dimensional (2D) material known for its remarkable conductivity,¹ intrinsic strength,² and other optoelectronic properties³ that have been investigated since its first reported isolation in 2004.⁴ Central to the use of graphene in a host of applications is the need to be able to functionalize it in a predictable way.^{5,6} To that end, several approaches have been described in the literature, including fluorination and hydrogenation alongside boron-nitride substitution,⁷ covalent functionalization with diazonium salts^{8,9} or perfluorophenyl azides,^{10,11} and various forms of cycloaddition reactions.^{12,13} While these approaches have been shown to be robust, in many cases it is desirable to localize reactions in order to take full advantage of graphene's properties. This has led to several approaches for patterning graphene in order to control effects such as plasmon scattering,¹⁴ as we have shown by the use of reacting pre-patterned self-assembled monolayers with graphene to disrupt its π -conjugation.¹⁵ Moreover, while other routes for patterning of graphene also exist using nanofabrication techniques, such as electron beam lithography,^{16–18} these are usually subtractive approaches, which obviate the advantages of chemical modification, and as such, the ability to carry out directed functionalization at specific locations still remains a significant challenge.

Recently, we and others have shown how mechanical distortions can alter the chemical reactivity of graphene.^{19–32} Interactions between graphene and substrates with different morphologies and surface chemistries can alter the material's physiochemical properties.^{8,33,34} Further, local strain induced in graphene has been shown to drive increased reactivity when it is deposited on substrates whose roughnesses have been engineered or modified with nanoparticle films^{26,30,35,36} or self-assembled monolayers (SAMs).^{15,37,38} Computational studies have shown that this effect arises from the changes in the nearest neighbor p-orbital axis vectors (POAV); as the electronic structure becomes more sp^3 -like for C atoms at the peaks of the mountains, the activation barrier for reaction is lowered.³⁰ Beyond increasing the proclivity for reaction, the altered electronic landscape of the distorted graphene also provides a thermodynamic driving force that induces preferential molecular

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migration on graphene's surface from areas of concave curvature (*i.e.*, the valleys) to regions of higher convex curvature (*i.e.*, the mountains) for both one- and two-legged molecular walkers.^{28,31}

Recent developments in the nanomaterials space have brought forth numerous multifunctional nano- and microelectronic devices with applications in sensing and flexoelectric systems. Here, scalable fabrication and enhanced functionality are central to translating new proofs of concept in materials design and functionalization to utile applications. Earlier developments in suspended graphene piezoresistive systems³⁹ laid the framework for improving mechanical stability and sensitivity in next-generation devices.^{40,41} Scaling to centimeter-scale resonators⁴² has followed, along with studies of heterostructure modeling and simulation for 2D transducers^{43–45} which emphasize the integration of nanostructured materials into wearable sensors and sensing platforms. The latest advances highlight material architectures that combine nanotechnology and materials engineering for next-generation electronic and sensing applications.^{46–49} Recently, there has been a notable progression from fundamental innovation toward scalable, application-specific nano- and microsystems. The work presented here poses a new iteration in this cycle, whereby a unique, mechanically-driven patterning technique of graphene can ultimately yield site-specific, microscale architectures that can be exploited for myriad applications.

To examine strain-induced reactivity for isolated single-layer graphene, we developed a 2D-materials strain reactor (2D-MSR) which affords *in situ* Raman microspectroscopy and atomic force microscopy (AFM).³² Using this instrument, the oxidation of a suspended graphene by water was investigated, whereby a backing pressure of water on the membrane was used to distort the material's surface. By applying mechanical strain to the suspended graphene, it was shown that the material could be oxidized by water. The reaction could be followed by Raman microspectroscopy to inform both local changes in reactivity and strain in the graphene lattice^{50–52} by tracking changes in the defect-induced D peak and shifts in the strain-sensitive G and 2D peaks over time. As the applied backing pressure induced bending across the entire membrane, reaction was not localized to a single area and occurred across the membrane wherever the out-of-plane strain was the greatest.

As described above, given that reactions with strained graphene were found to occur with the greatest proclivity at the regions of highest distortion, if the mechanical strain in the graphene could be localized, then a pathway to the mechanochemically-driven patterning of graphene could be established. To accomplish this, herein we describe the use of acoustic oscillations to drive chemical reactions with graphene. Here, by taking advantage of the 2D-materials strain reactor's AFM capabilities, we applied mechanical oscillations to induce standing waves in suspended bilayer graphene membranes as a means of creating regions of high distortion to induce reaction by treating the suspended graphene as a microscale drum. Using finite element modeling (FEM), we examined the frequencies at which high local curvature could be induced in these graphene "microdrums." Using these same frequencies, we experimentally demonstrate that location-specific hydrolysis could be achieved, with localized reaction confirmed by Raman microspectroscopy. The application of this acoustic approach opens the door to introducing specific reactions on graphene to afford the formation of features such as annular resonators.

RESULTS AND DISCUSSION

As described in the Methods section, in this work, bilayer graphene was suspended over 2-micron diameter pores on a supported TEM grid (Figure 1). To examine the wave dynamics of the bilayer graphene membranes, finite element modeling (FEM) was carried out to examine the frequency response of the membrane under an applied force at its center. Experimentally, an AFM tip was positioned at the center of a pore in air and resonated at an amplitude of 70 nm at the desired frequency while the underside of the membrane was in contact with water at pH = 7.

Finite Element Modeling (FEM) of Simulated Wave Propagation and Local Curvature

Using FEM, the dynamic response of a simulated graphene membrane to an oscillating loading force was modeled. After reaching steady state, the two-dimensional out-of-plane displacement field was analyzed as the primary indicator of the membrane's dynamic response. Representative two-dimensional displacement snapshots at excitation frequencies of 1, 10, 20, 50, 100, and 200 kHz are shown in Figure 2. At low excitation frequencies for 1–10 kHz, the membrane response is dominated by the fundamental vibration mode, producing a single displacement maximum near the membrane center. As the excitation frequency increases to 20–50 kHz, higher-order vibration modes begin to emerge, resulting in additional off-center displacement maxima. At 100–200 kHz, the displacement field becomes increasingly complex, exhibiting multiple off-center displacement maxima and annular features characteristic of higher-order membrane vibrations.

Representative time-dependent centerline vibration profiles extracted from the two-dimensional simulations are provided in the Supporting Information (Figure S1). As noted, it has been reported that curvature-induced strain can drive molecular migration and site-selective reactivity, with molecules preferentially localizing in regions of positive curvature.³¹ Therefore, we analyzed centerline height profiles extracted from the two-dimensional displacement fields together with their first and second spatial derivatives to quantify local deformation features relevant to mechanochemical activity. The first derivative

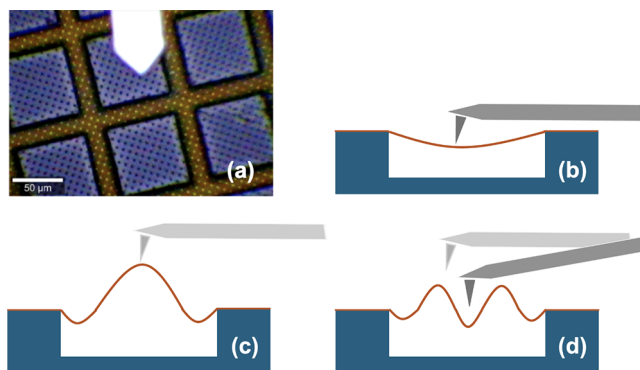


Figure 1. Schematic of the experimental setup. (a) Bilayer graphene on a TEM grid suspended over open 2 μm pores with an AFM probe in contact with the center of a pore. (b) Free-standing membrane with an AFM tip positioned at the center or the pore. (c) Oscillating at low frequency (1–20 kHz). (d) Oscillating at high frequency (>100 kHz). Water is introduced beneath the membrane, and imaged by confocal Raman microspectroscopy.

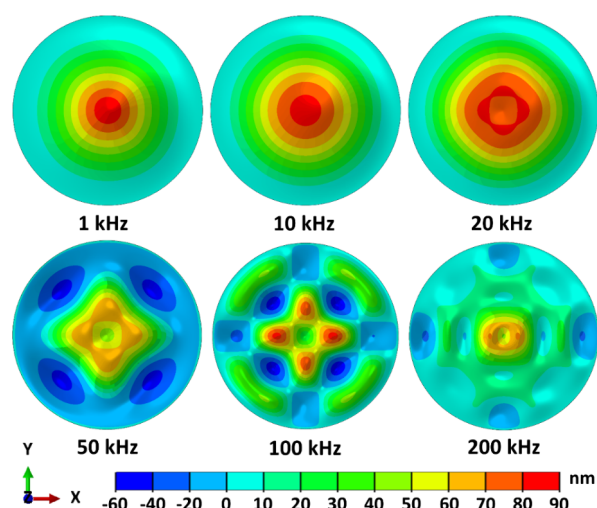


Figure 2. Representative two-dimensional out-of-plane displacement (height) snapshots of the suspended graphene plate at excitation frequencies of 1, 10, 20, 50, 100, and 200 kHz after the membrane has reached steady-state vibration.

quantifies the local slope of the height profile, while the second derivative highlights curvature, which is an important indicator of local lattice distortion and potential mechanochemical reactivity. Representative height, slope, and curvature profiles at 1, 50, and 200 kHz are shown in the [Supporting Information \(Figure S2\)](#). The red dotted lines indicate the locations of the largest absolute curvature, while the green dotted lines indicate the largest absolute curvature excluding the membrane center. At 1 kHz, the largest curvature occurs at the membrane center,

whereas at 50 and 200 kHz additional off-center curvature maxima emerges approximately 0.25 μm and 0.15 μm away from the membrane center, respectively, as higher-order vibration modes develop. The magnitude of the maximum curvature is also greater at higher frequency, increasing from approximately 1.2 $/\mu\text{m}$ at 1 kHz to 10.6 $/\mu\text{m}$ at 200 kHz (see [Supporting Information Figure S3](#)). Throughout steady-state vibration, these high-curvature regions persist over many oscillation cycles, although their positions evolve with time (see [Supporting Information Figure S4](#)).

These results indicate that both the magnitude and spatial distribution of high-curvature regions depend strongly on excitation frequency. To quantify this behavior statistically, the radial positions of all mesh nodes with an absolute curvature greater than 70% of the global maximum absolute curvature for each excitation frequency were identified over all steady-state simulation frames (see [Supporting Information Figures S4 and S5](#)). The resulting normalized radial distributions are shown in [Figure 3](#). At 1 and 10 kHz, the high-curvature regions are concentrated near the membrane center, consistent with the fundamental vibration mode. At 20 and 50 kHz, higher-order vibration modes begin to develop, producing additional off-center high-curvature regions while the center remains the dominant location. At 100 and 200 kHz, the high-curvature population becomes substantially broader and shifts away from the membrane center, reflecting the increasing dominance of higher-order vibration modes. This progressive redistribution of high-curvature regions is consistent with the experimentally observed transition from center-localized reactivity at low frequencies to annular (ring-like) reaction regions at higher frequencies.

The frequency ranges discussed in this work are specific to the 2 μm -diameter suspended bilayer graphene membranes

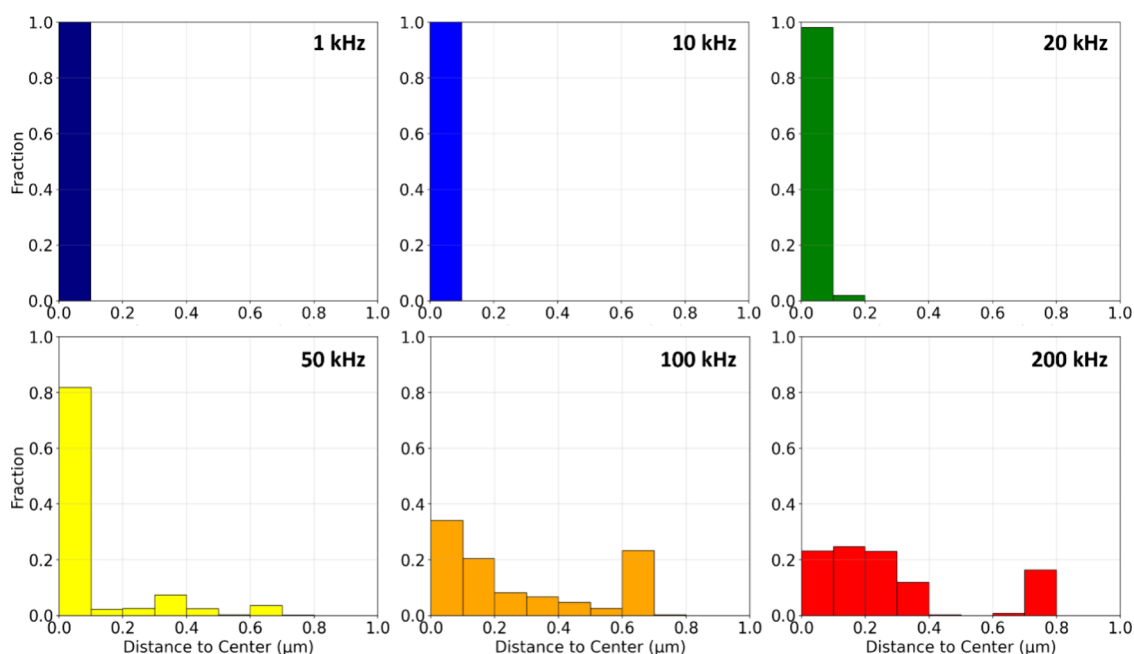


Figure 3. Histograms showing the distribution of the radial positions of the high-curvature regions during steady-state vibration at excitation frequencies of 1, 10, 20, 50, 100, and 200 kHz. For each frequency, the second spatial derivative of the out-of-plane displacement (curvature) was evaluated for all mesh nodes over all steady-state frames. Only nodes with an absolute curvature greater than 70% of the global maximum absolute curvature for that frequency were included in the analysis. The histograms show the normalized fraction of these high-curvature nodes as a function of distance from the membrane center.

used experimentally and are intended to describe the transition from a fundamental vibration mode to progressively higher-order modes. For translation to other pore diameters and different suspended materials, an eigenfrequency analysis was performed using the same geometry and properties of this system in the transient dynamic simulations. The fundamental axisymmetric bending mode was found at 8.45 kHz, while representative higher-order modes up to approximately 117 kHz were also shown to illustrate the evolution of the vibration patterns with increasing frequency (see [Supporting Information Figure S6](#)).

Reaction of Water with Resonated Graphene “Microdrums”

The FEM results established two regimes for experimental investigation: low (1–20 kHz) and high (100–220 kHz) frequency oscillations, suggesting that mechanochemical reactivity will be favored closer to the center of the graphene pore at lower frequencies and propagate further outward at higher frequencies. To validate this, an AFM probe was used to create ripples in individual pores of suspended bilayer graphene in contact with the underlying reactant medium (water). A pore was located and imaged prior to each reaction as a reference. Following this, the AFM probe was oscillated at the desired frequency for 1 h before ultimately acquiring a post-reaction Raman map. For each frequency, controls under dry conditions were also acquired to ensure that the reported changes to the graphene’s Raman spectral character were indeed reflective of chemical functionalization rather than mechanical wear caused by phenomena such as localized heating or fatigue from the extended period of tip oscillation. In the absence of the underlying water, no appreciable changes to the Raman spectral maps or extracted point spectra were observed. A representative comparison between a bilayer graphene membrane resonated in air (dry conditions) and over water can be found in the [Supporting](#)

[Information \(Figure S7\)](#), as can extracted point spectra comparing the D peak character in reacted and unreacted regions.

Following the predicted variation from FEM, the low frequency and high frequency regimes are clearly distinct from one another, as evidenced by the series of characteristic experimental Raman spectral maps in [Figure 4](#) which show the Raman D peak intensities at increasing frequencies. Extracted point spectra from these maps showing the D peaks and relating the I_D/I_G values are provided in the [Supporting Information \(Figure S8\)](#). At low frequencies, a central node could be clearly observed. At higher frequencies (*i.e.*, exceeding 100 kHz), bilayer graphene exhibited intense D peak signatures that, when rendered in three dimensions, clearly exhibit a ringlike zone of reactivity at the roughly predicted locations for the modes shown. Given the diffraction limited resolution of the microscope, the features show cross-sections of *ca.* 400 nm FWHM. These changes in the Raman spectral character following the applied resonance indicate that an oxygen-modified bilayer graphene surface is now present. Further spectroscopic analysis could provide further insights into the exact chemical nature of these modifications. Presently, we utilize these data as a proof-of-concept demonstration of our capacity to site-selectively alter the suspended graphene surface.

The transition from single-peak to multiple-peak vibrational patterns in the simulation, along with the similar observed experimental phenomena, can be explained by considering the timing between the applied load and the reflections from the fixed boundaries, together with the wavelength of the induced waves. At low driving frequencies, the load period is much longer than the travel time of waves reflecting from the pore edges. This means that the reflected waves return while the applied load is still in its early stages, leading to a weak temporal overlap between the incoming and reflected waves. In this regime, the bending waves are long compared to the size of the pore (or

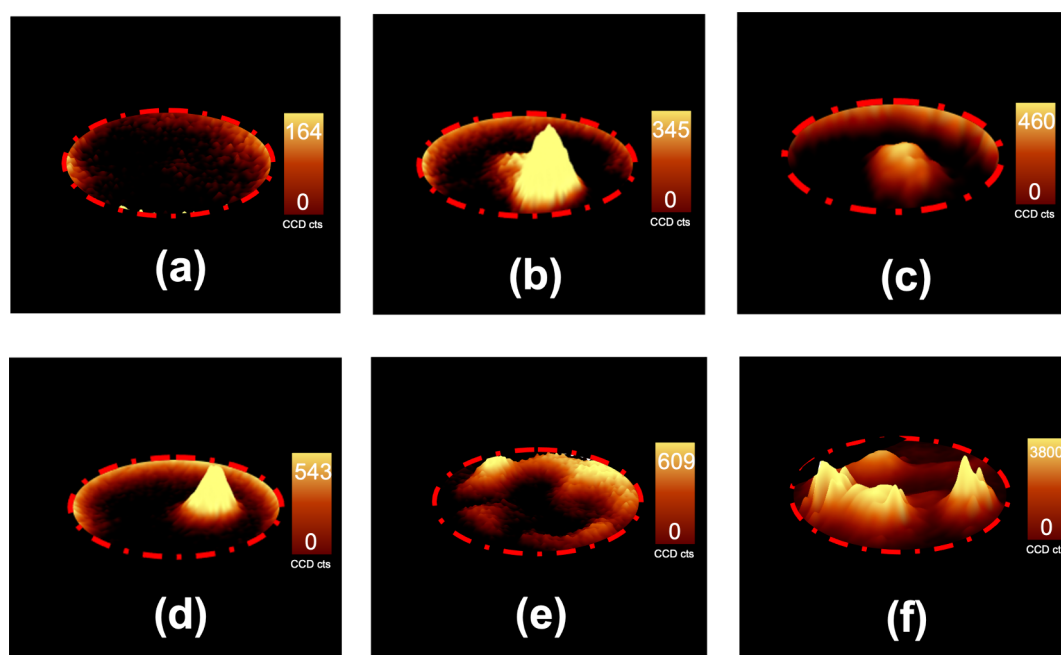


Figure 4. Representative Raman D peak intensity maps rendered in three dimensions following reaction of suspended bilayer graphene as a function of increasing probe oscillation frequency: (a) 0 kHz; (b) 1 kHz; (c) 10 kHz; (d) 20 kHz; (e) 100 kHz; and (f) 220 kHz. The red dotted lines indicate the perimeter of the graphene microdrum. Each microdrum is 2 μm in diameter.

simulated rod), so the deformation remains concentrated at the center; this produces a broad, centralized bulge that manifests as a single peak of maximum curvature in simulation and correlates to such a peak of reactivity in experiment.

As the frequency increases, this situation changes. Although the reflection from the boundaries remains the same, the load period becomes shorter; thus, the degree of overlap between the applied load and the reflected waves increases. The stronger overlap produces additional regions of constructive and destructive interference, allowing curvature maxima to emerge not only at the center, but also between the center and the fixed edges. At the same time, the bending wavelength decreases with increasing frequency, reinforcing this spatial distribution of curvature. Together, these effects cause the vibrational response to evolve into multiple displacement peaks across the suspended membrane.

Unlike static modal nodes in classical vibrational theory, these ringlike regions are dynamic; they oscillate continuously in response to the driving force, creating more complex spatial patterns at higher frequencies. Rather than affecting primarily the patterns induced in the graphene surface, tuning the applied frequency of oscillation alters the extent to which the material can be displaced from its initial plane. At higher frequencies, greater displacement and thus greater geometric alteration of the graphene occurs, resulting in the significantly higher extent of reaction based on the intensity of the D peaks that are detected in the Raman spectral maps. At lower frequencies, the regions of reactivity are clearly localized to being at or near the center of the graphene pore, in keeping with the distributions from the finite element modeling simulations.

CONCLUSIONS

In this work, we have demonstrated that suspended graphene micropores can serve as functional platforms for spatially controlled mechanochemistry *via* interaction with an oscillating AFM probe in the presence of a reactant medium (water). As the excitation frequency increases, the resulting pattern evolves from a central hotspot to concentric, ringlike motifs. Exploring alternative reactant media—such as those containing dienophiles or other selectively reactive species—could enable localized functionalization with chemical specificity. Importantly, this work highlights the potential of AFM-based acoustic actuation as a nontraditional tool to spatially program reactivity in two-dimensional materials. Similarly, applying mechanical distortions to graphene using very localized forces or, induced by depositing graphene on a patterned substrate to induce strain in a specific configuration, should permit directed functionalization, to enable facile spatially resolved mechanochemical functionalization of graphene and other atomically thin material systems. This is a meaningful step forward in developing a better understanding of the ways in which mechanical force can be used to facilitate chemical reactions.

METHODS

2D-Materials Strain Reactor

For the full parameters and specifications of the 2D-materials strain reactor (2D-MSR), in addition to the basic functioning of this tool, the reader is directed to Hawthorne *et al.*³² Briefly, the 2D-MSR is a modular tool that can be installed into the scan stage of an existing microscope for AFM and Raman characterization. With the 2D-MSR,

a solvent or gas is flowed at a controlled rate and pressure through a complete circuit, providing a backing pressure to an adhered 2D material and a medium with which it can react. In this work, the 2D-MSR was switched off once the water had made contact with the graphene membrane, allowing for the mechanical action of the oscillating AFM probe to dominate.

Materials

Bilayer graphene grown by chemical vapor deposition (CVD) that had been transferred to Quantifoil® electron microscopy (EM) grids were purchased from MSE Supplies. These EM grids were 12 μm thick with a 12 nm amorphous carbon support film with square arrays of circular 2 μm pores. These grids were adhered to the caps of the strain reactor using a two-part silver epoxy (EPOTEK H20E). A through-hole in the cap allowed for the solvent to come in contact with the center of the EM grid.

FEM Simulations

FEM was used to analyze the vibrational modes and dynamic behavior of the system. The suspended circular graphene in the experiments was approximated in FEM as a two-dimensional circular plate. The system was modeled in ABAQUS with a diameter of 2 μm and a thickness of 0.67 nm, corresponding to the reported thickness of graphene.² The plate was discretized using 89,176 linear tetrahedral elements, resulting in approximately 300 nodes along the membrane diameter. This mesh density was selected to provide sufficient spatial resolution for accurately capturing the frequency-dependent vibration modes and the associated out-of-plane displacement and curvature distributions while maintaining computational efficiency.

A material density of 2267 kg/m^3 was used based on reported values for graphite.⁵³ Anisotropic material properties were assigned to capture the directional mechanical behavior of bilayer graphene. Specifically, the elastic constants were defined separately for the in-plane (x-y plane) and out-of-plane (z-direction) responses of the graphene sheet. The Young's modulus was set to 1000 GPa in-plane⁵⁴ and 25 GPa out-of-plane.⁵⁵ The Poisson's ratio was 0.165 in-plane and -0.1 out-of-plane.⁵⁶ The shear modulus was 300 GPa in-plane and 2 GPa out-of-plane.⁵⁷

Periodic harmonic loading was applied along the z-direction over a small circular region at the center of the top surface of the graphene plate to simulate external excitation. The loading was defined as a sinusoidal function in time, with excitation frequencies of 1, 10, 20, 50, 100, and 200 kHz. A transient dynamic analysis was conducted to capture the system's time-dependent response to the applied periodic loads. Each simulation was run for a duration of 0.01 s, corresponding to 10, 10², 2 $\times$ 10², 5 $\times$ 10², 10³, and 2 $\times$ 10³ loading cycles and 5 $\times$ 10², 5 $\times$ 10³, 10⁴, 2.5 $\times$ 10⁴, 5 $\times$ 10⁴, and 10⁵ loading time steps for applied frequencies of 1, 10, 20, 50, 100, and 200 kHz, respectively. The maximum magnitude of the sinusoidal periodic load was 40 MPa. This duration was determined to be sufficient for the system to reach and maintain steady state vibration. We defined steady state as being reached when the transverse displacement of the center node exhibited periodic oscillations with a maximum amplitude variation of less than 2% across successive cycles. The resulting displacement profiles were recorded throughout the simulation, allowing for detailed analysis of vibrational behavior and its dependence on excitation frequency.

Acoustically Driven Reaction on Graphene

Graphene samples were subjected to the acoustically driven reaction *via* applied frequencies from an AFM probe (Value AFM Probes, Bruker, Model NCLV-A, 0.01–0.025 $\Omega\text{-cm}$ (n) doped Si) at *ca.* 1, 10, 20, 100, and 220 kHz. Raman spectral maps were acquired before and after reaction, assuring that any defects already present in the graphene were not mistakenly reported as being reflective of reactivity.

Atomic Force Microscopy and Raman Spectral Acquisition

The 2D-MSR was placed into the scan stage of a WITec confocal Raman-atomic force microscope (300RA). The microscope could be readily alternated between AFM and Raman modes. The system was equipped with a 488 nm diode laser, a UHTS 300 VIS spectrometer, and a cooled Andor EMCDD detector ($-60\text{ }^{\circ}\text{C}$). Laser intensity for all Raman spectral measurements was *ca.* 150 μW exiting the $100\times$ objective (Nikon E Plan, 0.9 NA). A 600 g/mm spectral grating was used (resolution 3 cm^{-1}). The strain reactor was placed into the microscope stage and a pore was chosen as near to the center of the grid as possible. An AFM image of a pore was acquired first so that the computerized scan stage could then be driven directly to the center of a pore. Once there, the probe was driven at the desired frequency for 1 hr.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.6c10502>.

S1: Vibrational simulations for all frequencies; S2: Centerline profiles for membrane height, slope, and curvature at selected frequencies; S3: Maximum simulated curvature as a function of frequency; S4: Maximum simulated curvature during steady-state vibration; S5: Steady-state out-of-plane displacement for off-center AFM probe; S6: Eigenfrequency analysis of vibrational modes; S7: Comparison of control and experimental conditions; and S8: Raman point spectra extracted from spectral maps at experimental frequencies; and Data Availability Statement (PDF)

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Author Contributions

Conceptualization and experimental methodology by E.J.B. and J.D.B. Conceptualization input from Y.B. and A.M.R. Experiments performed and data analyzed by E.J.B. and R.D. Computational modeling conceptualized by T.L. and A.M. and conducted by T.L. Written, reviewed, and edited collaboratively.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

AFM atomic force microscope
EM electron microscopy
FEM finite element modeling
2D two-dimensional
2D-MSR 2D-materials strain reactor

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