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Abstract: Optical microresonators have widespread application at the frontiers of nanophotonic technology, driven by their ability to confine light to the nanoscale and enhance light-matter interactions. Microresonators form the heart of a new method for single-particle photothermal absorption spectroscopy, whereby the microresonators act as microscale thermometers to detect the heat dissipated by optically pumped, non-luminescent nanoscopic targets. However, translation

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Optical microresonators, devices that confine light to microscopic volumes, have found widespread application within chemistry, biology, physics, and engineering.¹⁻⁵ A broad class of optical microresonators, whispering-gallery mode (WGM) resonators, have exhibited superb sensitivity including the detection of single nanoparticles,^{6, 7} single molecules⁸⁻¹¹ and even single metal ions.¹² However, the ability to perform spectroscopy on adsorbed objects would not only open a path toward label-free chemical identification, but also allow the interrogation of single object properties, free from the static and dynamic blurring of typical ensemble measurements. To this end, we recently employed microtoroid resonators as single-particle absorption spectrometers, whereby the heat dissipated by optically pumped nano-objects such as gold nanorods (AuNRs),¹³⁻¹⁶ carbon nanotubes,¹⁷ or conductive polymers¹⁸ is detected *via* small shifts in the WGM resonance condition. However, to harness the sensitivity of this method for chemically dynamic systems, a platform easily compatible with solution-phase measurements is necessary. Here, we report such a platform, the microbubble resonator, and use it to study the photo-activated chemical etching and reorientation of single AuNRs.

AuNRs¹⁹ have important chemical and biological²⁰ applications such as bioimaging,²¹ treatment of cancer^{22, 23} and infection,²⁴ label-free biosensing²⁵ down to single molecules,²⁶ surface-enhanced Raman spectroscopy,^{27, 28} fluorescence enhancement,²⁹ drug delivery,³⁰ and light harvesting to drive catalytic reactions.³¹ These applications heavily rely on tuning the morphology-dependent optical features of AuNRs, necessitating precise tailoring of their dimensions. This result can be achieved during AuNR fabrication, where seed-mediated synthesis³² can often tame the polydispersity that typically plagues samples. However, in many cases polydisperse AuNR samples are still common and post-synthetic modifications offer an attractive route to achieve a desired morphology. Furthermore, significant particle-to-particle variations of key optical properties of AuNRs both on surfaces³³ and in solution³⁴ highlight the heterogeneity within a population of nanoparticles, underscoring the need for single-particle inspection, including during nanoparticle synthesis and modification. A variety of optical methods exist for probing non-luminescent single nanoparticles and molecules *via* photothermal,³⁵⁻³⁸ scattering,³⁹⁻⁴¹ and other techniques.⁴²⁻⁴⁵ Observation of the chemical etching of single AuNRs has recently been accomplished with one-photon luminescence,^{46, 47} dark-field scattering,⁴⁸⁻⁵³ and liquid transmission electron microscopy (TEM).⁵⁴ However, a highly sensitive absorption technique for monitoring such chemical dynamics is needed to compliment these methods, and would be extremely valuable for accessing targets that are not luminescent or are too small for scattering experiments. WGM resonators are perfectly poised to fill this gap in methodology.

Various WGM microresonator geometries have been employed for sensing in solution, including microspheres,⁹⁻¹¹ microrings,^{5, 55} microtoroids,^{6, 56} microbubbles,⁵⁷⁻⁵⁹ microdroplets,⁶⁰ microtubes,⁶¹ and microbottles.^{62, 63} In particular, the variations and capabilities of hollow microresonators for sensing have been reviewed in detail elsewhere.⁶⁴ To adapt a microresonator for in-solution, visible-wavelength photothermal spectroscopy, three requirements must be met: (i) high sensitivity for interrogating nanoscopic analytes, (ii) resonator transparency at visible wavelengths to mitigate photothermal background, and (iii) robust performance in solution. Employing silica-on-silicon (SiO₂-Si) microtoroids for photothermal spectroscopy, one can resolve attometer shifts of the WGM resonant wavelength from thermal fluxes of target nano-objects.¹³ High backgrounds in SiO₂-Si toroids can be mitigated with all-glass microtoroids, which can be used for visible spectroscopy.^{15, 16} However, immersing a WGM microresonator in water mandates the use of larger microresonators to avoid bending losses,⁶⁵ with consequent lower

photothermal sensitivity. Furthermore, although tapers⁶⁶ and prisms⁹ can be optically coupled to WGM microresonators in water, immersion of such couplers in solution may reduce mechanical stability and also result in fouling, particularly as more caustic reagents are employed for chemical studies. Therefore, an alternative platform is preferable for in-solution experiments. The microbubble WGM resonator, **Figure 1B**, which possesses a hollow, solution-accessible interior, while maintaining an air-glass exterior interface, meets the requirements for in-solution, visible spectroscopy of nanoscopic analytes.

Microbubbles are fabricated from glass capillaries, resulting in low background signals at visible wavelengths, tunable fabrication, and two-port connectivity through which it is easy to flow reagents. Compared to a solid resonator immersed in solution, a microbubble maintains an air-glass interface on its exterior, enabling a higher refractive index contrast and allowing for smaller diameter resonators before bending losses occur. Additionally, the tapered optical fiber used for coupling light into the resonator can approach in air, reducing noise from the instability of coupling in-solution and eliminating solution contamination of the taper. Furthermore, the unique, thin-walled structure of the microbubble allows for high-order optical modes that exist almost entirely within the liquid-core of the resonator, a situation termed the “quasi-droplet regime”. Operating in the quasi-droplet regime, microbubbles have proven exceptional sensors, most recently for detecting polystyrene nanoparticles in aqueous solution with a sensitivity ~280 times larger than similar experiments using microsphere resonators.^{57, 58} Together, these factors make microbubble resonators ideal for time-resolved spectroscopy of single-particle chemical reaction dynamics when exposed to solution. In this paper, we introduce microbubble absorption spectrometers for probing and controlling the chemical and rotational dynamics associated with the photo-activated chemical etching of AuNRs. This platform holds promise for elucidating mechanistic insights into nanoparticle reactions with a method orthogonal to existing techniques that rely on scattering or luminescence, and is an attractive candidate for future single-particle and single-molecule studies.

Experimental Design:

WGM resonators operate *via* total internal reflection, wherein light propagates around a closed geometric loop, resulting in resonance conditions where only specific wavelengths propagate constructively. WGM resonances are interrogated by the “probe beam”, provided by a continuous wave (CW), narrow-linewidth, tunable laser coupled through a tapered optical fiber⁶⁷ (**Figure 1A**). Transmitted light through the tapered fiber is collected and the probe beam is actively locked to a resonance by a Pound-Drever-Hall locking system.^{6, 13, 68-70} The hollow core of the microbubble is filled with the desired reagents by attaching the microbubble capillary to a syringe pump. Two microbubbles are pictured in **Figure 1B**, highlighting the tunability of geometric parameters, and consequent versatility on optofluidic properties.

A second beam, the “pump beam”, is focused onto the microbubble surface to excite analytes. CW diode lasers at 532 nm, 635 nm, and 785 nm are coaligned using dichroic mirrors, permitting interrogation at different wavelengths. The linearly polarized pump beam is amplitude modulated at 433 Hz using an optical chopper, encoding the photothermal signal at this frequency and allowing for use of lock-in amplification to drastically lower the experimental noise floor.¹³ Two galvanometer mirrors steer the pump beam through a relay lens system to a 40x objective with piezo-controlled focus, providing spatial control of the pump beam on the microbubble resonator. This spatial control is leveraged to photothermally map the interior surface of microbubble resonators, at low resolution for an entire resonator, and high resolution for single diffraction-limited objects. **Figure 1C** shows two photothermal maps of a microbubble resonator at different objective foci, with the out-of-focus map indicating the curvature of the microbubble from the varied PSFs across the map. The polarization angle of the linearly polarized pump beam is rapidly scanned using a voltage-controlled liquid crystal, which is sandwiched between a polarizer and a quarter-waveplate (see **Methods**). This combination of wavelength, spatial, and polarization control permits thorough

characterization of individual analytes bound to the resonator, realized at exquisite sensitivity due to the double-modulation scheme.

Figure 1. Microbubble Absorption Spectroscopy. (A) Cartoon of instrumentation. PDH=Pound Drever Hall. LC=Liquid Crystal. APD=Avalanche Photodiode. (B) Optical micrographs of two microbubble resonators with different geometries. Scale bars 20 μm . (C) Photothermal maps of a microbubble resonator similar in geometry to the left microbubble in Figure 1B, both out-of-focus (left), and in-focus (right). Scale bars 20 μm .

Operation of Single-Particle Microresonator Spectrometers:

Microresonator sensing schemes generally rely on the reactive mechanism,¹⁰ whereby binding of an analyte imparts a small refractive index change, shifting the resonance wavelength. Instead, microresonator-based photothermal spectroscopy relies on a resonance shift resulting from the heat plume generated by optically pumping a non-emissive object bound to the resonator surface.¹⁷ The temperature rise accompanying this heat plume alters the resonator's refractive index according to its thermo-optic coefficient (dn/dT), changing the WGM optical path length and shifting the resonance condition. The ability to detect this resonance shift is related to the figure of merit Q/V , the ratio of the resonator's quality factor (Q) and mode volume (V). A resonator with minimized absorption, bending, and scattering losses allows photons to repeatedly circulate the resonator, resulting in a high Q , narrow linewidth resonance. This narrow linewidth increases the visibility of minute resonance shifts. A smaller resonator with consequent tighter confinement of light produces a smaller V , increasing the overlap between the thermal plume of the analyte and the optical mode. This increased overlap contributes a larger effective refractive index change and thus a larger resonance shift.¹⁷ To properly examine the microbubble photothermal response we employed finite-element simulations (COMSOL) of both the optical modes and the thermal properties of the microresonator. Simulated optical modes for a particular microbubble geometry are shown in **Figure 2A**. Varying mode numbers, defined in the traditional spherical geometric indices (polar, azimuthal, and radial, **Supporting Information**), clearly show the complicated mode structure inherent in the microbubble resonators. This complex mode structure gives rise to several important experimental considerations.

First, the efficient excitation of high-order modes leads to incredibly congested mode spectra. An illustrative 180 pm window of a water-filled microbubble's resonance landscape is shown in **Figure 2B**. This high mode density stems from the highly prolate resonator geometry lifting the polar mode degeneracy relative to an ideal spherical resonator,⁷¹ leading to varying effective resonator sizes for modes, as well as differing free-spectral ranges.⁷² The differing free-spectral ranges cause spectral overlap of modes of different azimuthal mode order,⁷³ an effect that is compounded by the disparate dielectric environments experienced by different-order radial modes, which have different fractions of the electric field contained in glass, water, and air. Second, the burrowing of higher-order radial modes into the water-filled interior not only changes the effective refractive index of the mode but also yields tremendous variations in dn/dT . This varied dn/dT , which can even switch signs, produces very different thermal responsivities for modes. The combined congested mode spectrum and differential shifting from dn/dT variation amplifies experimental challenges, as photothermal heating or ambient temperature drifting can cause modes to shift through each other. Therefore, modes that are both thermally responsive and spectrally isolable are desirable.

Choosing a high thermal responsivity mode requires delving into the expected thermal response with finite element simulations. As described above, the radial mode order drastically alters the effective dn/dT , as glass has a small positive dn/dT of $9 \times 10^{-6} \text{ K}^{-1}$ and water a large negative dn/dT of $-91 \times 10^{-6} \text{ K}^{-1}$. Thus, while glass-contained modes in a water-filled resonator offer Q values over 10^6 and show small positive resonance shifts upon heating, higher-order, water-contained modes offer Q values of mid- 10^5 and show large negative resonance shifts captured both experimentally (**Supporting Information**) and in our simulations in **Figure 2C**. The “shark fin” shape results from the pump beam amplitude modulation. Interestingly, this modulation rides atop a rising baseline magnitude as heat builds over many modulation cycles (left panel) before thermal equilibrium is reached (right panel). This baseline stems from the lack of an effective, proximal heat sink in microbubbles with equilibration reached only after sufficient heat dissipation to the air, yielding a baseline shift about ten times larger than the modulating shift, both experimentally and theoretically (**Supporting Information**).

Finding high-order water-contained radial modes to leverage their larger thermal response requires careful consideration of the coupling geometry. Specifically, the tapered fiber diameter⁷² greatly impacts mode selectivity through phase matching conditions and evanescent field overlap. By translating along the length of the tapered fiber this diameter was tuned until these water-contained modes were suitably excited. Then a thermally sensitive and spectrally isolated mode was selected by wavelength scanning. Importantly, the precise identity of this mode was not discerned, precluding direct relation of a resonance shift with an absolute absorption cross-section as in our previous experiments.^{13, 17} Identification is possible,⁷⁴⁻⁷⁶ particularly when implementing procedures to simplify the mode structure,^{73, 77} but difficult in practice and was not pursued here.

Importantly, this lack of mode identification precludes the selection of the maximally thermally responsive mode. While the optimal mode is required for ideal sensor response, use of a less responsive resonance was sufficient for examination of AuNRs. The limit-of-detection of our system was investigated by optically pumping a single AuNR inside a resonator. The photothermal signal, averaged for 30 s with a

Figure 2. Optical resonances in microbubble resonators. (A) Simulated electric field distributions at 780 nm for first, second, and third order radial modes, for both first and second order polar modes. All modes shown are Transverse Electric (TE). White curves are added to clearly indicate the position of the microbubble walls. (B) A 180 pm span of the mode spectrum of a microbubble resonator. (C) *Left:* The signal at the beginning of analyte pumping. *Right:* Signal once the resonator has reached a thermal equilibrium with its surroundings (theoretical). (D) Resonance shift from pumping a single gold nanorod with the 635 nm beam at decreasing powers (blue points). The red point indicates the signal for pump beam off. The inset is a zoom-out, showing signal linearity over orders of magnitude in pumping power. Further details in main text. Error bars are standard deviation of the mean.

time constant of 1 s (**Figure 2D**), was monitored at decreasing powers until it was indistinguishable from the signal obtained with the pump beam blocked. As the inset in **Figure 2D** shows, the signal remains linear over multiple orders of magnitude, flattening out at low powers as the noise floor is reached. The detection limit for this platform is in the low tens of attometers of wavelength shift (a comparison with microtoroids is made in the **Supporting Information**). For context, the typical photothermal response of a single AuNR at our pump fluxes is in the range of 10-100 fm, easily resolvable by many orders of magnitude. Additionally, this detection limit surpasses the expected femtometer photothermal shift for measuring a single chromophore.¹⁷ As a first step towards monitoring reaction dynamics of molecules, we show below that microbubbles are well-suited for probing the chemical and spatial dynamics of single AuNRs.

Probing photophysical features of single AuNRs:

AuNRs exhibit optical features known as localized surface plasmon resonances (LSPRs), which result from light exciting collective oscillations of conduction band electrons. Two orthogonal LSPRs exist in AuNRs: the longitudinal plasmon band (LPB) and the transverse plasmon band (TPB), oriented parallel and perpendicular, respectively, to the long axis of the rod (**Figure 3A**). The LPB is at the longer wavelength in the bulk extinction spectra of the AuNRs used in this report (80×40 nm), **Figure 3B**. These spectral features are probed with the microbubble platform detailed in **Figure 1A** at the single AuNR level, at specific pump beam wavelengths (solid vertical lines **Figure 3B**). The LPB central wavelengths will likely be red-shifted compared to the bulk due to interaction with the glass surface.^{39, 78, 79}

After depositing AuNRs inside of a microbubble resonator (**Methods**), the resonator is photothermally mapped to find objects. To confirm successful deposition of single AuNRs, photothermal maps are acquired with the pump beam, linearly polarized from 0 to 180 (**Figure 3C**) at three different pump wavelengths. These maps are fit to extract an intensity at each polarization (**Methods**), shown as data points in **Figure 3D**. These polarization dependent intensities are fit (dotted lines) to give a depth-of-modulation, M (**Methods**). The 635 nm and 785 nm traces, which probe the LPB, have a value of M close to unity for a single AuNR. A criterion of $M \geq 0.98$ was used for classifying an object as a single AuNR. Small well-ordered aggregates could also exhibit high M values, but these are unlikely due to the presence of CTAB during deposition. Alternatively, a much faster method of probing AuNR orientation is to rapidly rotate the pump beam's linear polarization while centered on an object, and fit the results to extract M . Although this method (**Figure 3E**) lacks background subtraction, it allows for hundreds of data points to be collected in a few seconds, resulting in quick determination of AuNR orientation and relative absorption cross-section at the pumping wavelength during reactions.

For both of the above polarization methods, the traces for the 635 nm and 785 nm pump beams align in peak angle (**Figure 3D** and **Figure 3E**) because both of these wavelengths excite the LPB. In contrast, the 532 nm trace has a peak angle orthogonal to the other two traces because this wavelength excites the TPB at a pump polarization orthogonal to the LPB excitation. In addition, the 532 nm trace does not go to zero, because at that wavelength the pump beam is not only pumping the polarization-dependent TPB, but also the interband transitions of gold, which are independent of pump beam polarization. Notably, the use of multiple wavelengths means that AuNRs can not only be localized, but also studied spectroscopically. Herein, these capabilities are employed to study the etching of AuNRs in real-time.

Selecting an etchant:

The photophysical properties of AuNRs are well understood as a function of geometry⁸⁰ and post-synthetic modifications are extremely useful for exerting control over these properties. Since 2002, when Jana and coworkers observed anisotropic etching of gold spheroids in both cyanide and persulfate solutions,⁸¹ at least 20 other reagents have been reported to etch or accelerate the etching of AuNRs, often with spatial selectivity (see **Supporting Information**). Such reports include assays for facile detection of

Figure 3. Probing photophysical features of single AuNRs. (A) Cartoon illustrating the photophysical features of a AuNR. LPB=Longitudinal Plasmon Band. TPB=Transverse Plasmon Band. (B) Bulk absorption spectrum of AuNRs, with the various laser beams in our experiment indicated by vertical lines. LPB and TPB indicated. (C) Example photothermal maps of a nanorod as pump polarization is varied in increments of 20 degrees, as shown by the red arrow in the cartoon above the photothermal maps. Scale bar 1 μm . (D) Polarization fits for three different pump beams acquired using photothermal mapping. (E) Polarization traces for three different pump beams, acquired by recording photothermal signal as the linear pump polarization is quickly rotated 180 degrees (~ 10 seconds).

analytes at ultra-low concentrations in both environmental and biological samples, indicating the utility of morphological control of AuNRs both in-the-field and at points-of-care.

Most of the aforementioned reports used spectrophotometers to study ensembles of AuNRs. Although some studies used TEM intermittently to verify nanorod morphology, this approach is limited in time resolution, and generally requires stopping reactions for analysis. Optical monitoring of reactions of single AuNRs can also be accomplished *in situ*. Dark-field spectral imaging has been used to study anisotropic etching of individual AuNRs by hydrogen peroxide,⁴⁹ potassium iodide/iodine,⁵⁰ and gold(III).⁵³ In a different experimental design, luminescence was employed to study the cyanide etching of AuNRs.⁴⁷ Additionally, dissolution of AuNRs *via* substrate voltage tuning has been monitored using dark-field hyperspectral imaging.⁴⁸ Perhaps the most commonly reported reagent for etching single AuNRs in recent years is iron(III) chloride, starting with bulk studies in 2009.⁸² Since then, FeCl_3 etching of single AuNRs

has been reported using dark-field monitoring, sometimes utilizing Le Châtlier's principle to drive the reaction.^{51, 52} Ferric etching of single AuNRs using an electron beam, monitored by liquid-TEM, has also been reported.⁵⁴ Excepting the electron beam study, these reports evoked purely chemical mechanisms to explain their reported chemistries. However, the light-induced etching of AuNRs using FeCl₃ has also been reported, both in bulk studies,⁸³ and single AuNR experiments using one-photon luminescence.⁴⁶ Due to significant interest in ferric etching of AuNRs and the intriguing mechanistic parameter space, FeCl₃ was employed for etching in this report.

Single AuNR Reactions:

After single AuNRs deposited in the microbubble resonator were identified, they were chemically etched using FeCl₃. The etching solution, ranging between 250 μ M and 2 mM FeCl₃ dissolved in dilute hydrochloric acid (pH~1.3) to prevent hydrolysis of the oxidant, was flowed into the microbubble. Due to differences in sensitivity resulting from microbubble geometries, mode selection, and even nanorod location within the same microbubble, the relative photothermal signals between nanorods cannot be directly compared. However, the relative signal of one AuNR reacting over time, using the same resonance, directly maps onto a change in absorption cross-section of the nanorod at the pump wavelength, and thus its etching progress. Conveniently, nanorod etching was found to be photo-activated by the pump beam illumination (discussed further below), allowing controlled reaction initiation. The AuNRs were monitored by repeatedly rotating the linearly polarized pump, interrogating the relative absorption and orientation of the AuNR as it is etched. Importantly, before each polarization trace is taken, a beam-centering algorithm is used to mitigate any false signal decrease from spatial drift of the bubble. The centering also serves as a “dosing” period to enable AuNR etching between polarization traces.

Figure 4A (i-iii) features three exemplary traces of a single AuNR reaction (additional examples in the **Supporting Information**). These three reactions were taken in different microbubbles on different days, confirming reproducibility of the experiment. A logarithmic version of reaction (i) (**Figure 4B**) readily shows the late stage continued reaction progression along with AuNR rotation. This behavior is better illustrated in the extracted maximum signal and angle traces from reaction (ii) seen in **Figure 4C** and **Figure 4D** respectively. The reactions slowed as they progressed, as seen by the plateauing effect in the maximum signal. This plateauing is a direct result of the photo-activation mechanism: as a nanorod shrinks, its absorption cross-section decreases, resulting in less light absorption and thus slower etching. This photo-activation is further confirmed by incrementally increasing the pump power (dotted vertical lines), quickening the reactivity before plateauing once again. Although the three reactions in **Figure 4A** were taken at ferric chloride concentrations spanning almost an order of magnitude, the time scales of reaction vary by much less (discussion in **Supporting Information**). It is also evident that AuNRs sometimes rotate as they etch, especially late in reactions, as seen in **Figure 4D** and discussed later (see **Single AuNR Rotations**).

A control experiment was performed with a nanorod-containing resonator filled with dilute hydrochloric acid (pH~1.3) without FeCl₃, confirming that the acid alone is not enough to etch the nanorods under illumination. Additionally, when nanorods are left in etching solution for multiple days without laser illumination, they do not observably react, supporting a photo-activated etching mechanism. AuNRs exposed to etching solution for hours within a microbubble, with the probe beam on and locked to water-dominated modes but no pump beam, also did not undergo significant etching, indicating that the probe beam is not sufficient to drive etching. Therefore, we hypothesize a photo-activated mechanism resulting from hot electrons generated from LPB decay (see **Mechanistic Discussion**). We also note that, occasionally, nanorods were “impervious” to photo-activated etching, as discussed further in the **Supporting Information**.

To exemplify the spectroscopic versatility of this platform, nanorod etching was also induced with the 532 nm pump beam. Because this wavelength pumps the TPB (as well as direct interband transitions), nanorod orientation can still be tracked. In **Figure 5A**, a single AuNR reaction time series is shown for 532 nm-driven (TPB-driven) conditions, with a logarithmic version of the data shown in **Figure 5B** for clear visualization of late-stage etching data. The polarization traces are conspicuously different than in Figure 4 because of the presence of polarization-independent interband transitions. In **Figure 5C**, maximum signals are extracted for this reaction and one other TPB-driven reaction in the same resonator. For direct comparison, a different nanorod in the same microbubble was reacted using the 635 nm pump beam (LPB-

Figure 4. Etching single AuNRs. (A) Reaction series of polarization traces for three different reactions, progressing in time from red traces to blue traces. Maximum signal is normalized by pump flux. (B) The data for reaction (ii), but with signal shown logarithmically. (C) Maximum signal of polarization traces over the course of reaction (ii), showing the decrease in relative absorption cross section at 635 nm. Dashed lines indicate points in time at which pump power was increased. (D) Maximum angle of polarization traces over the course of reaction (ii), showing nanorod orientation. Dashed lines indicate points in time at which pump power was increased. Reaction conditions: dilute aqueous HCl (pH~1.3), room temperature, varied FeCl_3 concentrations (i) 1mM, (ii) 250uM, (iii) 2mM. Pump fluxes for reaction (i) were 2.7, 6.7, 11.4, 21.0, and 34.5 kW/cm^2 . Pump fluxes for reaction (ii) were 4.1, 11.9, 35.4 kW/cm^2 . Pump fluxes for reaction (iii) were 6.4, 15.9, 31.6, 57.3, 121 kW/cm^2 .

driven), with the extracted maximum signals shown in **Figure 5D** (note, this is the same reaction shown in **Figure 4A (iii)**). Overall, three such reactions were performed for each color in the same resonator to confirm reproducibility (**Supporting Information**). Although quantitative comparison of reaction rates between experiments is difficult due to the decreasing rate as absorption cross-section diminishes, it is clear from the extracted maximum signals that while the etching rate of the 532 nm-induced reactions is faster than the rate of the 635 nm-induced reactions, it is not multiple orders of magnitude faster, in contrast to previously reported bulk measurements, discussed further below.⁸³ The shapes of maximum signal traces for the LPB-driven and TPB-driven reactions are noticeably different, with the LPB-driven reactions yielding a concave up shape, and the TPB-driven reactions yielding a concave-down (**Figure 5c (i)**) or even

Figure 5. Etching reactions driven at two different pump wavelengths. (A) The reaction of a single AuNR being driven with the 532 nm pump beam, progressing in time from red traces to blue traces. Maximum signal is normalized by pump flux. (B) The same data as in (A), but with signal shown logarithmically. (C) (i) Maximum signal of polarization traces for the reaction shown in (A). (ii) A similar trace for a different nanorod reacted in the same bubble using the 532 nm beam. Dashed lines indicate time points at which pump power was increased. (D) Maximum signal of polarization traces for the reaction of a nanorod in the same bubble, but using the 635 nm pump beam to drive the reaction. Dashed lines indicate time points at which pump power was increased. Reaction conditions: dilute aqueous HCl (pH~1.3), room temperature, 1mM FeCl₃. Pump fluxes for reaction (Ci) 16.1, 39.2, 63.3 kW/cm². Pump fluxes for reaction (Cii) were 6.4, 31.6, 57.3kW/cm². Pump fluxes for reaction (D) were 6.4, 15.9, 31.6, 57.3, 121 kW/cm².

sigmoidal shape (**Figure 5c (ii)**). With the above data in mind, the hypothesized mechanism of photo-activated etching in these experiments will now be discussed.

Mechanistic Discussion:

For many reported etching reagents, a simple redox analysis predicts that AuNR etching should not be spontaneous. Though the oxidation potential for gold nanorods can be significantly lower than that of bulk gold,⁸⁴ it has nonetheless been demonstrated that additional reagents are typically required to modulate reactivity. For example, CTAB at concentrations above the critical micelle concentration (CMC) facilitates Au(III) etching of AuNRs, presumably by complexing with Au(III) and preferentially aggregating near AuNR tips.⁸⁵ CTAB dependence was also observed in the first report of FeCl₃ etching of AuNRs, including at CTAB concentrations well below the CMC, and was hypothesized to be due to the complexation of bromide from CTAB and chloride from FeCl₃ with gold, lowering its oxidation potential.⁸² In the single AuNR reactions in this report, oxidant concentration is two orders of magnitude lower than bulk studies showing light-independent etching (**Supporting Information**). This means that any halide dependence from CTAB or FeCl₃ is negligible in comparison to the much larger chloride concentration from the dilute

Figure 6. Proposed mechanistic explanation for etching rates. A slow initial step requiring CTAB dissociation before ferric ions can bind determines the overall rate for the reaction, muting the effect of the higher rate for TPB excitation, even though hot electrons are more efficiently generated. Eventually, etching stops when the absorbed light falls below a threshold necessary for hot-electron-driven etching.

hydrochloric acid. In conjunction with the studies discussed below, it is evident that CTAB plays an important role beyond halide donation.

In the bulk study by Toste and co-workers,⁸³ etching was multiple orders of magnitude faster when driven with interband excitation than with LPB excitation, a phenomenon attributed to differences in the generated hot electron distributions. This chemistry was accomplished with CTAB concentrations above the CMC. In contrast, in the single AuNR etching reported by Khatua and co-workers,⁴⁶ CTAB was thoroughly stripped from the surface of the nanorods using ozone. Using only a green laser to drive etching, which excites both the TPB and interband transitions, the authors then exhibited bidirectional control over the AuNR aspect ratio, attributed to a balance of thermally driven and hot electron driven mechanisms. In our work, CTAB was removed from solution and reduced at the surface of deposited nanorods by flowing water following deposition (**Methods**). However, due to the gentle nature of this approach, we speculate that our conditions are at an intermediate surface CTAB concentration between reports from Khatua and Toste. We hypothesize that this intermediate CTAB concentration results in a hot electron etching mechanism that is different than in the above reports.

Interest in hot carrier chemical processes has exploded in recent years in a variety of applications,⁸⁶ especially photocatalysis,⁸⁷⁻⁸⁹ with a particular emphasis on harvesting solar energy for driving chemical reactions. The mechanisms of hot carrier generation and transfer have been extensively studied,⁹⁰⁻⁹² including the hot carrier energy distribution's dependence upon excitation wavelength.⁹³ Notably, significant efforts have been made towards untangling the contributions of hot carrier effects and photothermal effects in both nanoparticle synthesis⁹⁴ and plasmonic photocatalysis,⁹⁵ as well as mapping hot carrier driven catalytic reactions on the surfaces of nanorods.^{96, 97} Although there are still significant unresolved questions in understanding plasmon-driven chemistry, the mechanisms of hot carrier transfer can generally be predicted by modeling the energy overlap between the hot carrier, the molecular orbitals of the adsorbed molecule/atom, and the fermi level of the metal.⁹⁸

Hot carriers likely play a dominant role in the chemical etching of AuNRs in the microbubble. With a temperature rise at the nanorod's surface expected to be under 1 K,⁴⁶ the observed etching mechanism should not be significantly influenced by photothermal heating, as with the higher power reactions in

Khatua's report.⁴⁶ With no noticeable dark reaction rate, and a photothermal mechanism ruled out, a hot carrier mechanism, whereby the decay of LSPRs or excitation of interband transitions result in hot electrons that can transfer to ferric ions on the nanorod surface, must be invoked to explain the observed reactions. Hot electrons, which have been driven out of thermal equilibrium to a higher energy than their ground state, lower the Gibbs free energy of the etching reaction,⁵² favoring products. The change in energy level of reactants also reduces the thermal activation barrier for electron transfer to ferric ions, modifying the forward rate constant and thus the reaction kinetics.⁹⁵ Specifically, photoexcitation of gold nanoparticles has been shown to lower the activation enthalpy for transferring electrons from gold nanoparticles to Fe^{3+} , and the dependence of this process upon excitation wavelength and power has been studied.⁹⁹

When the LSPRs of an AuNR decay, hot electrons are generated from the conduction band of the nanorod. These hot electrons are on average at lower energy than those generated by interband transitions, though a few carriers will be hotter in the LSPR decay case.⁸³ Toste and coworkers found that the larger population of lower-energy hot electrons generated from interband transitions drove ferric chloride etching of AuNRs orders of magnitude more efficiently than those generated from the LPB.⁸³ However, given that the TPB-driven reactions in this report proceed at a rate that is comparable to the rate of the LPB-driven reactions (**Figure 5**), we conclude that the etching mechanism observed here is fundamentally different than that observed by Toste.⁸³ Ultimately, the reaction relies on ferric ions binding to the nanorod before hot electron transfer can take place. Thus, a plausible mechanism entails a two-step process, whereby slow ligand exchange of CTAB with Fe^{3+} , or intercalation of the Fe^{3+} through the CTAB, is followed by fast photoactivated etching. A relative increase in the rate of the photoactivated step is then ultimately masked in the observed rate due to the slowness of the first ligand exchange step, as shown **Figure 6**. In the limit where ligand exchange is slow, increases in the rate of the photo-induced step would give a somewhat muted effect on the overall reaction rate, as observed. Intriguingly, it has been shown with single silver nanoparticles that photoexcitation can promote weakening of ligand-nanoparticle bonds, thereby lowering the energy barrier for reactions at the nanoparticle surface.¹⁰⁰ If such an effect exists for CTAB-coated AuNRs, it might also be dependent upon excitation-wavelength, resulting in differences in the observed kinetics of LPB-driven and TPB-driven reactions.

To further understand the shape of the reaction profiles, we modeled the spectral changes of the TPB and LPB for a nanorod being etched (**Supporting Information**). This simulation was done for a variety of etching schemes, from tip-only etching to side-only etching. Modelling was able to reproduce the concave-up shape observed in the LPB-driven reactions (**Figure 4C**). However, no combination of variables was able to capture the concave down or sigmoidal trend seen in some TPB-driven reactions (**Figure 5Ci and ii**), or fully reproduce the threshold behavior observed. Thus, with a completely linear reaction mechanism ruled out, we can speculate on possible origins of non-linearity in the etching mechanism. One possible origin of non-linearity stems from the evolution of nanorod morphology over time. For example, it was observed by Khatua that for certain laser powers, nanorod LPBs would red-shift, then blue-shift. Another possible origin derives from the changing concentration of CTAB, with a relatively dense coverage providing competitive inhibition for ferric ion binding at early times but AuNR etching resulting in easier access at later times. Future studies utilizing multiple pump beams could be valuable in studying these complex kinetics, as the evolution of the relative signal of the LPB and TPB excitation beams would yield important insight into the reaction mechanism. Thus, our new microbubble platform gives a path forward for spectroscopic mechanistic studies into the wavelength-dependence of hot-carrier driven chemical dynamics in single plasmonic nanoparticles.

Single AuNR Rotations:

Beyond using our microbubble spectrometer to monitor and control nanoparticle size, we can also use it to monitor and control nanoparticle orientation, adding significant utility to the microbubble

spectrometer platform. Indicated by the shift in peak polarization during etching reactions (**Figure 4** and **Figure 5**), AuNRs can rotate while etching. Alternatively, active rotation can be induced with the pump beam, allowing for control over nanorod orientation. This control results from the optical torque exerted by linearly polarized light on an anisotropic, absorbing plasmonic structure (**Figure 7a**), a phenomenon that has been demonstrated experimentally¹⁰¹ and theoretically,^{102, 103} and is discussed further in the **Supporting Information**.

Theory predicts that the optical torque acting on the AuNR from the 635 nm pump beam will align the AuNR perpendicular to the polarization of the incident beam. Indeed, this perpendicular alignment is exhibited upon sufficient excitation power. In this way nanorod orientation can be controlled to within approximately 10 degrees (**Figure 7b**) as AuNR orientation is stepped through a ~180 degree rotation. This control was accomplished by monitoring the photothermal signal, dislodging the nanorod with a large optical torque above some threshold incident power, and dithering the polarization until the photothermal signal was minimized at the desired polarization angle. This thresholding behavior was demonstrated further by a stepwise ramping of the pump laser intensity, resulting in an upward staircase of photothermal signal, until rotation was finally induced. As can be seen in the examples in **Figure 7C**, two different nanorods required significantly different pump powers to dislodge them from the microbubble surface.

Figure 7. Orientation control of single AuNRs. (A) A cartoon illustrating the optically induced torque that a AuNR experiences under illumination with linearly polarized light, both from side-view (*top*) and top-view (*bottom*). (B) A series of pumping experiments showing optical control of nanorod orientation. (C) Trace showing the photothermal signal as two different AuNRs are pumped at increasing laser powers until the AuNRs dislodge slightly from the resonator wall and rotate, eventually settling down off-axis of the polarization.

Following dislodgment, the signal quickly stabilized to around 70% of the maximum signal for the left nanorod trace, whereas it behaved semi-stochastically for the right trace, before settling at <40% of the maximum signal. These differences in orientational dynamics highlight the differences in the local environments around the two nanorods, including both Coulombic effects and refractive index differences. These staircase experiments were performed repeatedly for both nanorods in **Figure 7C** to confirm reproducibility (**Supporting Information**).

Light-induced rotation during reactions was observed more frequently as AuNR etching progressed. Likely, as Coulombic attractions between the AuNR and the resonator's surface were weakened, hydrodynamic or optical torques were allowed to rotate the AuNR. Although rotation events could be forced in water-filled resonators, higher pump thresholds were generally required, and AuNRs were immune to rotation at powers that would result in rotation in ferric chloride solution. Therefore, it appears that the presence of etchant reduces the Coulombic attraction between nanorods and the resonator wall, possibly through charge screening, permitting facile rotation. Though optical rotation of nanorods has been seen in previous experiments, the coupling between evolving surface chemistry and propensity for rotation has not been explored to our knowledge.

Radiation pressure and optical gradient forces could also influence AuNRs, affecting the rotation power threshold. However, varying the pump beam focus position, which would change forces along the optical axis, did not significantly impact rotation thresholds. Therefore, it appears that the torque described above is the dominant driver of nanorod rotation. Although scattering forces in three-dimensional trapping can orient anisotropic plasmonic nanoparticles parallel to the optical axis of the excitation beam,¹⁰⁴ one would expect this to result in a highly stochastic signal over time in the polarization traces of **Figure 3** and **Figure 4**, as well as a revival of signal upon shutting off and turning back on the pump beam. Such behavior was not observed. Therefore, AuNRs likely remain parallel to the plane of the resonator's surface during rotation, rotating only in two dimensions.

Conclusions and Outlook:

We have demonstrated microbubble resonators as a robust platform for studying chemical dynamics in solution *via* single-particle absorption spectroscopy. We used a microbubble spectrometer to observe changes in the optical properties of AuNRs as they were controllably etched by ferric chloride *via* a photo-induced mechanism. Additionally, we monitored and controlled the orientation of the AuNRs using optical torque. With this demonstration, we lay the groundwork for studying more complex reaction dynamics of single particles and molecules. Thus, this technique provides a complementary measurement to the luminescence and dark-field methods previously used to observe similar reactions as reported here. In particular, the demonstrated exquisite sensitivity offers prospects of examining non-emissive objects inaccessible with fluorescence and too small to observe with scattering, which scales as $1/\text{Volume}^2$, a more severe penalty than in absorption measurements, which scale more favorably as $1/\text{Volume}$. Furthermore, rotational control could be used to estimate Coulombic forces attaching deposited objects to the resonator, helping to understand the interface between nanoparticles and the surface. This knowledge, combined with structured light field manipulation of nanoparticles,¹⁰⁵ might be used to arrange arrays of plasmonic nanoparticles as desired. We believe that optical control of plasmonic nanoparticles within a microbubble resonator will yield new paths for in-solution, photonic-plasmonic assembly, and live-control of emergent optical properties in such coupled systems. Additionally, by providing a direct thermal readout, our method could be used to untangle the respective contributions of photothermal heating and hot carrier generation for nanoparticle reactions, aiding the design of improved nanocatalysts. Overall, there is a compelling case for the use of microbubbles in materials studies, sensing, and chemical kinetics, and even hybridizing them with plasmonic or acoustic sensing schemes for further applications. Microbubble absorption spectrometers thus hold great potential for pushing the frontiers of absorption spectroscopy at the nanoscale.

Methods:

Microbubble fabrication: Microbubble resonators were fabricated according to the method reported by Yang and coworkers.¹⁰⁶ First, a glass capillary (Polymicro Technologies, TSP250350) is tapered using a heat-and-pull method, until it is approximately 25 μm in diameter. Next, counter-propagating CO_2 laser beams are focused onto the capillary while positive pressure is applied from the inside of the capillary using an inert gas. The heat from the laser beams softens the capillary, allowing for the local expansion of the capillary to 50-100 μm in diameter, depending on the experimental parameters. Eventually, radiative cooling from the expanded glass outcompetes the expansion process, and the bubble's size stops increasing. To operate in the quasi-droplet regime, a wall thickness close to the wavelength of the laser beam used for WGM excitation is desirable. Microbubble wall thickness is determined by an equation reported by Henze and coworkers,¹⁰⁷ and validated separately by others.¹⁰⁸

Tapered optical fiber fabrication: Single-mode optical fiber was purchased from Corning (HI 780C). Tapered fibers are made by removing the polymer sheath, cleaning the fiber, and tapering using a heat-and-pull method with a hydrogen torch and motorized actuators (Thorlabs Z825B) until the fiber returned to single-mode, as determined using a 785nm diode laser (Thorlabs LPS-785-FC) and optical power meter.

Instrumentation for photothermal spectroscopy: A tunable, ultra-narrow linewidth, fiber-coupled CW laser (Newport TLB-6712) with a wavelength range of 765-781 nm was used for coupling into resonators. Pound-Drever-Hall locking electronics were constructed as previously reported,¹³ except for the use of a different voltage-controlled oscillator (Mini Circuits ZX95-310A+) and different lithium niobate phase-modulator (EOSPACE PM-0S5-01-PFA-PFA-765/782). PDH feedback was applied to the tunable laser using high-speed servo controller (Newport LB1005). The optical output from the experiment was collected using an APD (Thorlabs APD430A), and the photothermal signal was extracted using a lock-in amplifier (Ametek 7265). The resulting signal was collected using a Data Acquisition (DAQ) card (National Instruments BNC2120) for later processing. Custom LabVIEW code was used for instrumentation control. For photothermal mapping, a lock-in time constant of 20 ms or 50 ms was used. For polarization traces, a lock-in time constant of 50 ms was used.

Diode lasers were used for pump beams, with the wavelengths 532nm (FTEC2 532-20), 635 nm (FTEC2 635-50), and 785 nm (Thorlabs LPS-785-FC). The pump beam was amplitude modulated using an optical chopper system (Thorlabs MC200B), and steered using galvanometer mirrors (Thorlabs GVS212) run by outputs from the DAQ mentioned above, modified using custom electronics. The pump beam was focused using a piezo-controlled (Thorlabs DRV517) objective (Nikon Plan 40x, 0.65 NA). Pump beam polarization was controlled using a three-optic system, comprised of a linear polarizer (LPVISE100-A), followed by a liquid crystal variable retarder (Thorlabs LCC1423-A, LCC25) with its fast axis set 45 degrees relative to the polarization axis, followed by a zero-order achromatic quarter-wave plate (Thorlabs AQWP05M-600) with its fast axis set 45 degrees relative to the liquid crystal's fast axis. In this design, tuning of the liquid crystal voltage results in a rotation of linearly polarized light at the output of the three-optic system.

Polarization Plots: Shown in Figure 3C and Figure 3D, AuNRs are first identified by photothermally mapping them at different pump polarizations, and processing these maps with a 2D-Gaussian fit, which results in background subtraction. Then, the maximum signals for each plot are together fit to provide a depth-of-modulation (M), using equation (1), which also gives the maximum signal (σ_{max}) plotted in Figure 4C, and the polarization angle of the maximum signal (θ_{max}) plotted in Figure 4D.

$$\sigma(\theta) = \sigma_{\max}(1 - M * \sin^2(\theta - \theta_{\max})) \quad (1)$$

For the data in Figure 3E, the liquid crystal is used to rapidly collect many data points that are then fit to equation (1) to obtain M. This method does not include background subtraction.

Bulk/UV-Vis Studies: The bulk absorption spectrum in Figure 3B was taken using a UV-Visible Spectrophotometer (Varian Cary 50). Additionally, studies were conducted to confirm the effects of CTAB concentration and FeCl₃ concentration on bulk nanorod etching. The effects of added NaCl were studied to further examine the impacts of chloride concentration. Results and further discussion are in the **Supporting Information**.

Nanorod deposition in microbubbles: All chemicals were purchased through Sigma-Aldrich unless otherwise noted. To deposit nanorods in a microbubble, a 500x serial dilution is made of AuNRs (Nanopartz A12-40-650-CTAB-DIH-1-25) in a solution of 200x diluted HCl and 25 uM CTAB in water. The low CTAB concentration prevents nanorod aggregation during deposition, but keeps the CTAB concentration well below the CMC of ~1mM. Dilute hydrochloric acid, which results in a pH of around 1.3, encourages binding of the nanorods on the resonator interior by enhancing Coulombic interactions.⁹ For deposition, water is first flowed through the resonator using a syringe pump attached to the first port of the resonator's capillary. Then, dilute HCl is flowed through the resonator to prime the glass surface for deposition. Next, deposition solution is backfilled through the second capillary port, which is cut to a much shorter length to reduce deposition of AuNRs to the capillary's interior walls. Following this, dilute HCl is flowed through the resonator, followed by water, through the first port of the capillary to push out the deposition solution while maintaining a pH gradient. Water is flowed through the resonator for at least several minutes to ensure the removal of non-bound objects, and remove excess CTAB from the nanorod surfaces.

Reactions in Microbubbles: All chemicals were purchased from Sigma-Aldrich. Reaction mixtures are made by dissolving and serial diluting ferric chloride hexahydrate in 1/200 dilute hydrochloric acid, resulting in a solution pH of around 1.3. While reaction solution was flowed into the bubble, resonances shift as the refractive index being probed by the WGM changed. Complete filling of the microbubble with reaction mixture is indicated when the resonances have stopped shifting. Following this stabilization, the syringe pump pressure is released, resulting in a microbubble primed for etching experiments.

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Supporting Information Available:

- Geometric parameters of microbubbles, COMSOL simulations, comparison with microtoroids, static offset vs. modulated signal, mode shifting for different dn/dT values (experimental), modeling of LPB and TPB during etching, thermal expansion, diagram for mode indices, additional single AuNR etching data, additional rotation data, bulk reaction results, brief discussion on extracting reaction kinetics, background on AuNR etchants, impervious nanorods, theory of nanorod rotation, Matlab code for modeling plasmon changes during etching.

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