Supporting Information:

Gold nanorod plasmonic upconversion microlaser

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1 Materials Synthesis and Properties

1.1 Nanorod synthesis

First the gold nanorods (NRs) are synthesized in water via the seed mediated method. The seed solution is formed by mixing 5ml CTAB (0.2M), 5ml HAuCl₄ (0.5mM) and 600μl of NaBH₄ (0.01M) together. Afterwards, 5ml CTAB (0.2M), 125μl AgNO₃ (8mM), and HAuCl₄ (1mM) are combined serially. Then 70μl of L-Ascorbic Acid (0.788mM) is introduced to the growth solution. Finally, 12μl of the previously detailed gold seed solution is added, and the solution is left on a hotplate set at 45°C for 3hrs. The freshly made gold nanorods are centrifuged and washed by DI water twice to purify the solution.

They are re-suspended in 5ml DI water. Then, 10mg of mPEG-thiol (M.W. 5K, Laysan Bio) in degassed water is added to the solution and sonicated for 30s to mix thoroughly and reacted for 2hrs on a shaker. Finally the -SH functionalized nanorods are centrifuged and washed by methanol twice and re-suspended in toluene.

1.2 Nanorod film deposition

Polymethylmethacrylate (35k molecular weight, PMMA, Sigma-Aldrich) is added to the nanorod solution to reach 0.5% weight. Finally, the nanorod-PMMA film is deposited on the surface of the device by spin coating at 4000rpm for 1min. The nanorod-PMMA coated toroid is annealed in a gravity oven at 150°C for 2hrs to remove any residual solvent and thermally reflow the polymer film. Based on previous work, when these synthesis parameters (polymer and nanoparticle concentrations) are used, polymer films of approximately 30nm are achieved, as measured with multi-wavelength ellipsometry. Based on these film thickness and the SEM images, it is expected that all of the nanorods would be parallel to the surface.

To study the dependence of the threshold power and Q on the nanorod concentration, additional nanorod solutions are also made by serially diluting the initial solution (C_i). Specifically, five concentrations are made with dilution factors (F) of 1, 0.75, 0.5, 0.38 and 0.125, where the dilution factor is defined as $C = F * C_i$.

1.3 Nanorod Emission

To characterize the dependence of the nanorod on the refractive index, a series of measurements were performed with the nanorods suspended in water (n=1.333), methanol (n=1.316) and toluene/PMMA solution (n=1.486). For reference the refractive index of PMMA at 780nm is 1.485. The results are plotted in Figure S1. As can be observed, the emission wavelength clearly red-shifts as the refractive index increases.

Figure S1: Dependence of emission wavelength on refractive index of solution. All solutions are excited at 780nm.

This trend is critical to understanding the shift in emission wavelength that is observed between Figures 4 and 5 in the main text. The fluorometry data is taken in a solution of PMMA and toluene. However, the lasing data is taken with the nanorods embedded in a polymer film. Therefore, because the refractive index changes, it is not surprising that the emission wavelength would also change.

2 **Finite Element Method Details**

To thoroughly study the role that the polymer layer plays in the plasmonic laser system, we perform a series of finite element method simulations in which the polymer layer thickness and refractive index is varied, and its effect on the plasmonic resonance is quantified.

2.1 FEM details

We use COMSOL Multiphysics finite element method to model the plasmonic enhancement of the circulating optical field. The gold nanoparticle is placed on the central part of a slice of the resonator with an arclength of approximately $\lambda/2$ with mirrored faces, where λ is the resonant wavelength (Figure S2).

Figure S2: Schematic of FEM model.

Throughout all of the simulations, the following parameters are held constant. Based on the devices used in the experimental work, the minor (r) and major (R) radii of the simulated toroid are fixed at 4 μm and 26 μm , respectively. The distance (d) between the edge of the device and the gold nanoparticle is 13 nm and the thickness of the polymer film (t) is 24nm. The refractive index of silica is defined as 1.452, and the real and imaginary parts of gold are extracted from the table in [1].

To get acceptable accuracy, the size of the mesh elements are chosen to be 0.5, 50 and 3 nm in the gold nanoparticle, near the optical mode and in the thin layer. For the rest of the simulation region, including the air around the WGM device and the regions of the WGM device far from the fundamental mode, the mesh element size varied from 3.6 to 360nm.

To study the effect of the thin polymer layer on the optical field profile, the refractive index of the thin layer (t=24 nm) is changed. To allow the model to be generalized to other polymers beyond PMMA (n=1.485), the refractive index is varied from 1 to 1.6 in increments of 0.1.

2.2 Calculation of the effective mode radius

Based on the FEM results, we are able to study several different parameters of the system. For example, we can convert the refractive index and calculate the effective mode radius using the following formula:

$$r = \frac{\int r |E|^2 dr}{\int |E|^2 dr}$$

2.3 Effect of polymer thin film on the device behavior

By increasing the refractive index of the polymer thin film, the eigenvalue of the cavity decreases (Figure S3). In other words, as the refractive index of the polymer layer increases, the mode moves towards the outside of the toroid. Consequently, the resonance wavelength increases. This result is expected based on fundamental resonator physics and provides one method of validating that our model is working correctly.

Figure S3: The dependence of the cavity frequency on the refractive index of the coating.

As the refractive index of the coating increases, the maximum field inside the toroid decreases (Figure S4). This trend indicates that the mode is pushed towards the outside of the toroid where it interacts more strongly with the scattering point (nanoparticle). As a result, the Q drops and the field enhancement decreases.

Figure S4: As the coating refractive index increase, the maximum mode field inside the toroid decreases.

While the intensity of the field is dependent on the film refractive index, the radius of the maximum field inside the WGM device is independent of the refractive index of the polymer layer (Figure S5). This result indicates that the thin layer around the device acts as a perturbation and the field pattern inside the device is not significantly changed.

Figure S5: The dependence of the field size on the coating index.

As shown in Figure S6, by increasing the refractive index of the polymer layer from 1 to 1.486, effective mode radius increases by a negligible amount (24.8nm). Given the $\Delta R/R$ (change in radius/radius) is less than 0.09%, we can assume that the effective mode radius is not modified by the polymer layer, and the 24nm thick film has almost no effect on the dynamics of the resonance. However, if a thicker layer was used, the behavior would be different.

Figure S6: The dependence of the effective mode radius on the coating refractive index.

By increasing the refractive index of the polymer layer, the evanescent tail of the optical field of the microcavity is able to interact with the scattering points (gold nanoparticles). Therefore, the Q factor decreases. This decrease in Q results in a corresponding decrease in

field enhancement. By analyzing the field intensity at the surface of the nanoparticle, the relationship between plasmonic field enhancement and film refractive index can be determined (Figure S7). This relationship shows that in order to achieve maximum enhancement, the coating with the lowest refractive index should be used.

Figure S7: Dependence of plasmonic enhancement on coating index.

The results from our simulations direct us towards the fact that presence of the thin layer of PMMA does not modify the mode shape and resonance field enhancement and it could be assumed as a constant perturbation to the whole experiment and therefore the analysis could be done without taking the thin PMMA layer into account.

3 Experimental Measurement Details

3.1 Experimental set-up

An overview of the device test and measurement set-up is shown in Figure S8. To measure the Q of the cavity, the set-up shown in Figure S8a is used. To measure the lasing threshold, a minor adjustment is made, and the set-up shown in Figure S8b is used.

Figure S8: The testing set-ups. a) To measure the quality factor, the light from the laser is coupled into the resonator using a tapered optical fiber and is detected using a photodetector. The signal is recorded using a PCI digitizer/oscilloscope which is integrated into the computer. The laser wavelength is controlled using a GPIB card and function generator, also integrated into the computer. The coupling between the waveguide and resonator are visualized using top and side view machine vision systems. All data and images can be recorded using the computer. B) To detect and record the lasing emission, the side view camera is replaced by the fiber coupled spectrograph. The signal from the spectrograph goes to the computer for data acquisition. All other components operate as previously described.

The quality factor of the device is measured by coupling light from a tunable narrow linewidth laser centered at 765nm (Velocity series, Newport) into the cavity using a tapered optical fiber waveguide. Tapered fiber waveguides are a low loss (high efficiency) method for coupling light into and out of optical cavities. The tapered waveguide is aligned with the cavity using a high precision 3-axis nano-positioning stage and is monitored on top and side view machine vision systems. This approach allows the coupling between the resonator and the waveguide to be precisely controlled, and all coupling regimes (under-coupled through critically coupled) can be achieved. In the present series of experiments, where both Q and laser thresholds are measured, this ability is particularly important.

The transmission spectrum is recorded using a high speed digitizer/oscilloscope (National Instruments) in the under-coupled regime. During the quality factor measurements, the laser scan rate and range are controlled using a function generator and are optimized to minimize any nonlinear effects (eg thermal) which might distort the shape of the resonance. The loaded Q is calculated by fitting the spectra to a Lorentzian and using the expression $Q = \lambda / \delta\lambda$, where $\delta\lambda$ is the full-width-half-max determined from the fit.

To characterize the lasing behavior, the side view camera is replaced with a fiber coupled spectrograph (Andor), and the fiber is aligned with the toroid. The testing set-up is enclosed in a black-out curtain, and a background measurement is performed before beginning the experiment and is used to normalize the threshold measurements. The lasing threshold is determined by changing the input power to the toroid using an optical attenuator. The maximum detectable signal on the spectrograph is 65,000 counts. As a control measurement, a non-functionalized silica toroid is also characterized.

The input power is the power which is coupled into the resonator. This power is distinct from several other power values, such as the circulating power in the resonator or the power from the laser to the waveguide-cavity system. The input power takes into account the amount of the laser power which is coupled into the resonator. For example, at critical coupling when 100% of the power is coupled into the resonator, the coupled input power would equal the laser power. However, in the majority of our experiments, approximately 50% of the power from the laser was coupled into the cavity; therefore, the coupled power was similarly decreased.

3.2 Calculation of circulating power

The circulating power (P_{circ}) in the cavity is proportional to the quality factor, device diameter and the input power. It is the reason that higher Q devices with smaller diameter have lower lasing thresholds. The circulating power is theoretically described by:

$$P_{\text{circ}} = P_{\text{in}} Q \frac{\lambda}{\pi^2 n R} \frac{\kappa}{(1 - \kappa)^2}$$

where κ is the coupling coefficient, λ is the wavelength, R is the device radius, P_{in} is the input power, Q is the quality factor, and n is the effective refractive index. The coupling coefficient can be determined from the transmission spectrum (T) using the below relation:

$$T = \frac{(1 - \kappa)^2}{(1 + \kappa)^2}$$

4 Quality factor measurement

4.1 Effect of nanoparticles on quality factor

The quality factor is a sum of all of the losses in the resonator, including the scattering loss, absorption loss, radiation loss and coupling loss. In previous work using spherical nanoparticle coated cavities, it was demonstrated that the absorption loss is dominant. The expression for Q_{mat} is: $Q_{\text{mat}} = 2\pi n / \lambda \alpha$, where n and α are the effective refractive index and effective absorption or material loss, which incorporate the refractive index and material loss of the silica, the nanoparticle-polymer coating and air. The optical loss can be determined from the UV-Vis measurements. In the present work, the same trend was observed, with Q decreasing in proportion to $1/\alpha$.

5 Dependence of threshold on nanorod density

The plasmonic laser behaves analogously to a dye laser. Therefore, similar equations describing the threshold can be applied. Specifically, the lasing threshold ($\gamma(\lambda)$) can be described by:

$$\gamma(\lambda) = \frac{n_1}{n_t} = \frac{2\pi n / \lambda Q(n_t) n_t + \sigma_{abs}(\lambda)}{\sigma_{abs}(\lambda) + \sigma_{emis}(\lambda)}$$

Where n is the refractive index, n_1 is the number of excited plasmonic particles (on-resonance) and n_t is the total number of plasmonic particles per unit volume, $\sigma_{abs}(\lambda)$ and $\sigma_{emis}(\lambda)$ are the absorption and emission cross sections, and Q is the quality factor of the cavity. Therefore, an increase in the number of excited particles can decrease the threshold. However, because an increase in the number of plasmonic particles decreases the Q , by increasing the material loss, there is an optimum balance between high particle concentration and high Q factor.

In Figure S9, this balance is clearly evident. The Q factors of the devices ranged from $7E5$ to $8E7$. However, lasing was only observed in the middle three concentrations, due to the balance between Q and concentration.

Figure S9: The dependence of quality factor and lasing threshold power on the nanoparticle dilution factor.

- [1] E. D. Palik, Handbook of Optical Constants of Solids (Elsevier Science & Tech, 1998).