Supporting Information

Plasmonically enhanced Kerr frequency combs

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Number of pages: 8

Number of figures: 6

Experimental details: nanoparticle synthesis and device fabrication

Gold Nanorods (Au NRs)

The gold nanorods are synthesized in water via a seed mediated method. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \bullet 3H_2O$), sodium borohydride ($NaBH_4$), L-ascorbic acid, cetyltrimethyl-ammonium bromide (CTAB), and silver nitrate ($AgNO_3$) were used as purchased (Aldrich). Thiol-terminated polyethylene glycol (PEG-SH, MW=2 kDa) was purchased from Polymer Source Inc. and used as received. Ultrapure deionized water (DI) was used for all solution preparations and experiments. Glassware was cleaned by soaking in aqua regia and washed with DI water.

The seed and the growth solutions are prepared as presented in the Methods section. Afterwards, 4 mL of 0.004 mM PEG-thiol was added to the dispersed Au NRs solution. The reaction was mixed for 2 h, separated by centrifuging, and the supernatant was discarded. To remove residual and untreated PEG-thiol, the solution was centrifuged at 9000 rpm for 15 m and re-mixed 3 times with water and methanol. The PEGylated Au NRs were redispersed in methanol and the concentration was adjusted to 2.5 mM. Fig. S1a shows an SEM image of the dispersed gold nanorods on a Si surface and the corresponding optical absorption spectrum in solution.

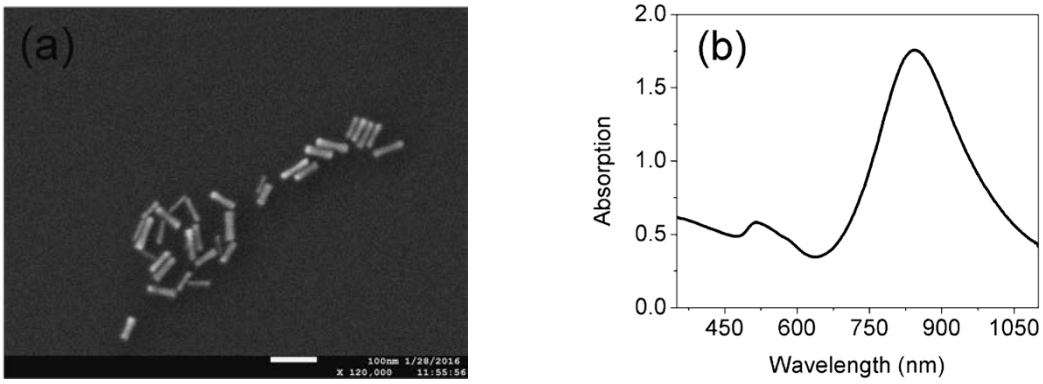

Figure S1. (a) SEM image of the gold nanorods used in the experiment to decorate the optical resonator surfaces. (**b)** UV-Vis spectrum of the colloidal solution in methanol.

Fig. S1a shows gold nanorods with transverse and longitudinal lengths of 13.10 ± 4.13 nm and 57.58 ± 12.75 nm, respectively. In addition, the shape and size is confirmed by using UV-Vis spectroscopy. The spectrum in Fig. S1b presents the two characteristic plasmon absorption bands of gold nanorods centered at 530 nm and 845 nm, corresponding to the transverse and longitudinal modes.

Silica resonant cavities

The silica spheres are fabricated by melting a tapered optical fiber using a CO_2 laser. Standard optical fiber (SMF-28, Newport) is initially tapered to a diameter of 40 ± 5 μm. It is then irradiated using the CO_2 laser for 2 s, causing the silica to form the spherical cavity. This process results in a uniform and atomically smooth surface. Tapered fibers with diameters of 40 ± 5 μm result in spherical resonators with diameters of 135 ± 5μm.

Surface attachment

The SiO_2 resonator surface is exposed to an O_2 plasma for five minutes to clean and hydroxylate the surface. This treatment increases the hydrophilicity of the surface, improving the efficiency of the nanorod attachment. The nanorods are applied to the resonator surface using a dip-coating method. The resonator is immersed in the colloidal solution for 30 seconds and then slowly removed. Fig. S2 displays a set of SEM images from the dip-coated resonators. The distribution of gold nanorods for two different nanorod concentrations is shown.

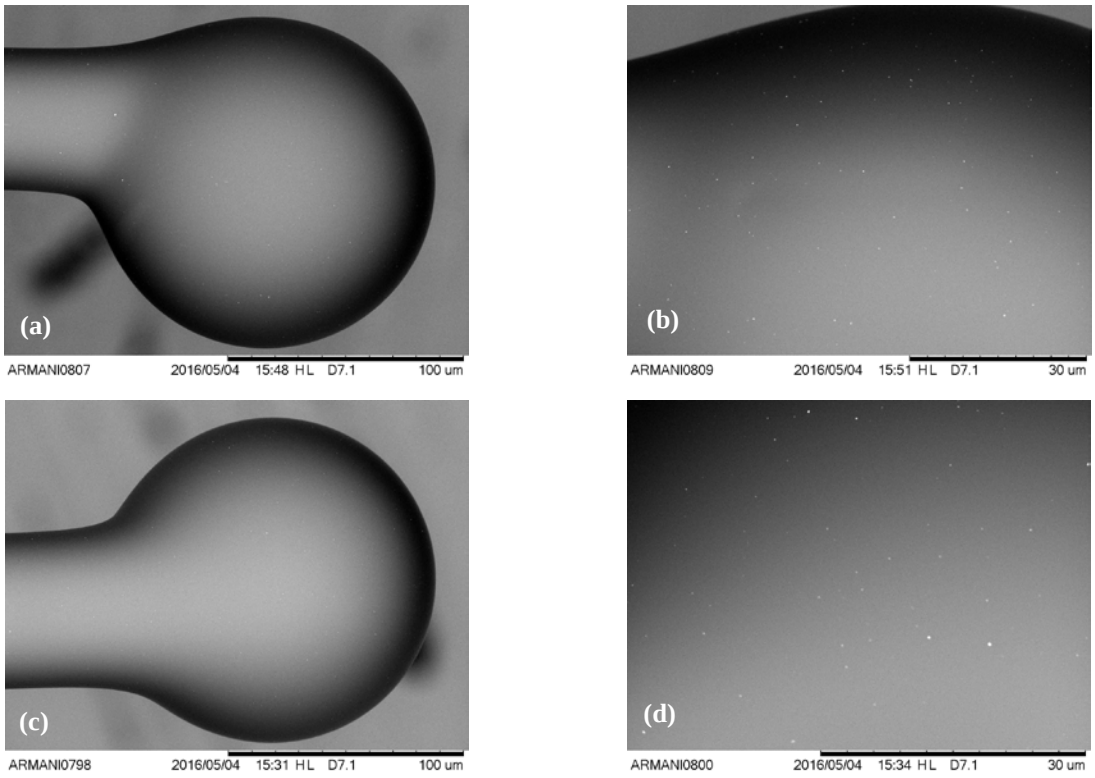

Figure S2. The gold nanorods are distributed homogeneously on the surface of the silica resonators at concentrations of (**a**) 0.125 mM and (**c**) 0.80 mM. (**b**) and (**d**) show higher magnification images of the same devices as in (**a)** and (**c**), respectively.

The imaging was performed with a Hitachi TM3000 SEM equipped with a de-Gausser, which allows for resolving the metal nanoparticles on the insulating silica resonator surface. From the SEM images, it is apparent that the coating procedure leaves the SiO_2 cavities with a smooth surface, allowing for the Q factor to remain high.

Simulation details

In order to study how the gold nanoparticles behave at off-resonant wavelengths, we incorporated particles in multiple finite element method 3D simulations and studied the field enhancement at a wavelength of 1550 nm.

Finite Element Method

We use COMSOL Multiphysics finite element method (FEM) to model the hybrid modes supported in the cavity by the dielectric-metal device configuration.

The simulation consists of an arc of the resonator, where the arc length is half of the resonant wavelength inside the resonator. The two sides are mirrored to enforce zero field condition (Fig. S3). The gold nanoparticle is placed at the center of the arc at a distance d from the surface. Both the plasmon-polariton field and the hybridized mode between surfaces are modeled.

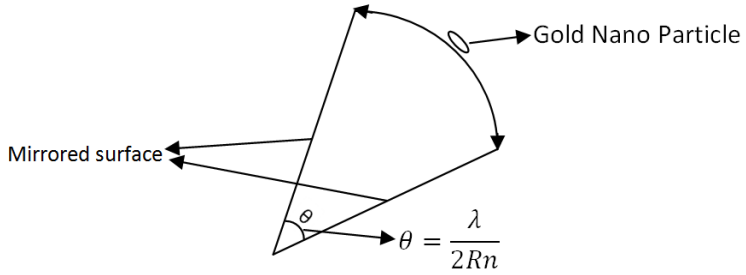

Figure S3. Schematic representation of the FEM model used to study the field enhancement.

The structure is meshed with the following scales: the resonator is meshed with maximum of λ/10, the nanoparticle is meshed with a maximum mesh size of 5 nm, and the polymer filling the area between the nanoparticle and the resonator is meshed with a mesh size of 10 nm, which enables us to study the effect of the thin polymer layer on the mode. In the small region between the gold nanoparticle and the resonator where the field is maximum, we have decreased the mesh size to be 0.5 nm in order to improve the accuracy. The refractive index for PEG was chosen to be 1.5. The

purpose of including a thin layer of PEG in the simulations is to study the effect of PEG on the mode characteristics and the local field enhancement.

It is challenging to incorporate the PEG layer into the model. It is not possible to only cover the gold nanoparticle with a thin layer of PEG because this configuration would require an extremely small mesh size, resulting in unreasonably long computational times. Additionally, because the refractive index of the polymer is higher than that of the resonator, the entire surrounding environment cannot consist solely of the polymer. In order to overcome these problems, we uniformly covered the resonator with the thinnest possible layer of PEG that did not require ultra small mesh sizes. This layer completely covered the region between the gold nanoparticle and the resonator. To achieve this goal, we used a 35 nm layer of PEG.

Device Characterization

An overview of the optical set-up used to measure both the fundamental optical properties of the device and its third order optical parametric response is shown in Fig. S4. To measure the parametric behavior, a beam splitter (BS) (90:10) is added to the system, sending 10% of the signal to the oscilloscope and 90% to the optical spectrum analyzer in order to study the third order nonlinear signals from the device.

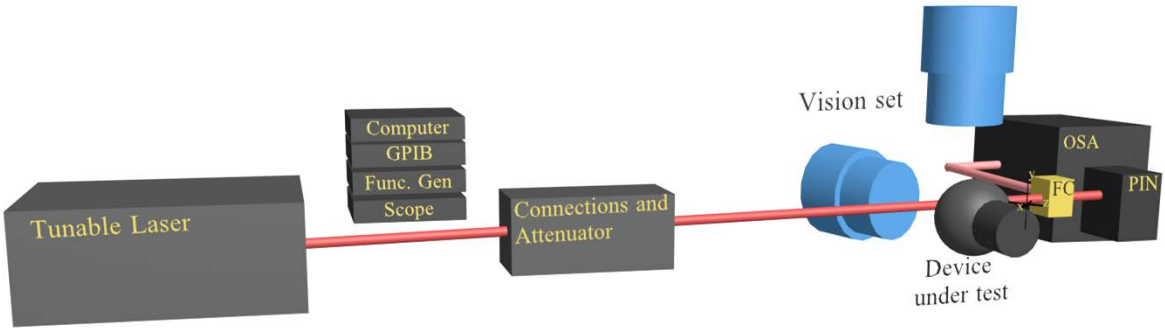

Figure S4. The testing setup allows for both the quality factor and the nonlinear optical signals to be recorded in parallel by splitting the optical signal from the device and simultaneously analyzed using a PCI digitizer/oscilloscope integrated into the computer and an optical spectrum analyzer (OSA). The laser wavelength is modulated using a function generator (FG).

Optical characterization

Light is coupled from a tunable narrow linewidth laser centered at 1550 nm (Velocity Series, Newport) into the optical resonators using a tapered optical fiber. To ensure optimal coupling

between the tapered fiber and the optical resonator, the resonator is positioned on an xyz motorized nanopositioning stage with a resolution of 20 nm. Additionally, the position between the device and the tapered fiber is monitored by a pair of optical imaging systems positioned at the top and the side (vision set). Thus, both the nanopositioning stage and the camera systems allow us to properly align the devices and to optically excite the whispering gallery modes on the equatorial plane of the sphere. Additionally, by changing the gap distance between the cavity and the waveguide, the amount of optical power coupled into the cavity can be controlled.

By modulating the laser wavelength with a function generator, the Q factor is measured by recording the transmitted power of the device in the near-zero coupling regime using a high-speed oscilloscope. By fitting the resonance to a Lorentzian, the full width at half-maximum ($\delta\lambda$) is determined and the loaded quality factor is defined by $Q = \lambda/\delta\lambda$. The laser scan rate and the range are controlled using a function generator (FG) and are optimized to isolate the resonance and minimize thermal effects. The intrinsic Q is determined by recording the transmission spectra over a range of coupling conditions (taper-cavity gap distances) and by using a coupled resonator model to isolate the extrinsic (coupling) losses from the intrinsic cavity Q.

To characterize the third order nonlinearity of the device, the emission spectra (frequency comb and Raman emissions) are recorded on an optical spectrum analyzer (Yokogawa AQ6370). All of the measurements are taken from 1400 nm to 1700 nm with 50,000 points recorded at a resolution of 0.05 nm.

The parametric threshold is determined by changing the input power to the hybrid optical resonator. For control and comparison purposes, we also tested 1) a bare silica optical resonator and 2) an optical resonator coated with non PEG-functionalized gold nanoparticles to study the effect of PEG on the nonlinear behavior of the device. The waveguide-cavity gap distance (cavity photon loading) was held constant across all of these measurements.

Correlation factor calculation

The relationship between the signal and idler power is linear, with a correlation factor of ~0.95±0.03.

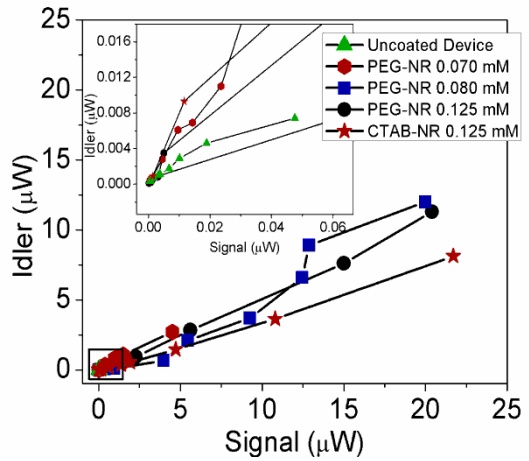

Figure S5. The relationship between the signal and idler power is linear, with a correlation factor ~0.95±0.03 for the resonators coated with PEG-functionalized nanorods. Inset: The results at low Signal:Idler powers. At the power used in the present work, the uncoated resonator did not exceed this range.

Peak intensity and circulating power calculations

To compare the performance of the Kerr effect in different optical devices, the power circulating inside the device (P_{circ}) is calculated using:

$$P_{circ} = P_{in} Q \frac{\lambda}{\pi^2 n R} \frac{K}{(1+K)^2}$$

where λ is the resonance wavelength, R is the device radius, P_{in} is the input power coupled into the device, Q is the quality factor of the device, n is the effective refractive index and K is the coupling coefficient. K is directly related with the transmission spectrum (resonance wavelength) as follows:

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

In addition, peak intensity circulating into the cavity is presented as the P_{circ}/A_m, where A_m represents the mode area of the TM mode supported in the cavity. Note that we have used the definition for the mode area that originates from energy considerations. Also, we have assumed that the optical mode is highly localized. The mode area is defined as:

$$A_m = \frac{\int \varepsilon(r)|E|^2 dA}{\max(\varepsilon(r)|E|^2)}$$

This value can be calculated from the previously discussed FEM simulations.

For the case of third order nonlinearities (e.g. Raman, OPO) the nonlinear gain is inversely dependent on another effective mode area where the spatial overlap between the signal and the pump is taken into account. In such a case, the effective nonlinear mode area is defined by:

$$A_{eff} = \frac{\left(\int_{A_{total}} |E_P|^2 dA\right)^2}{\int_{A_{cavity}} |E_P|^4 dA}$$

where the integral in the numerator is taken over the entire volume (internal and external to the resonator) for normalization of the fields. The integral in the denominator is taken only over the resonator media where nonlinear phenomena take place, namely in the silica, gold, and PEG. Note that A_m is used to calculate the intensity and A_{eff} is used to calculate the threshold of nonlinear process.

For comparison purposes, the thresholds for parametric behavior are calculated using the required peak intensities in each optical device.

Comb Generation in Non-Functionalized Gold Nanorod-Coated Resonators

For the resonators coated with CTAB-coated gold nanorods, the span of the frequency comb is ~250 nm at input circulating intensity of 1.85 GW cm^{-2}. Without the presence of the nonlinear molecule between the gold nanorod surface and the resonator surface, the OPO process is not as efficient.

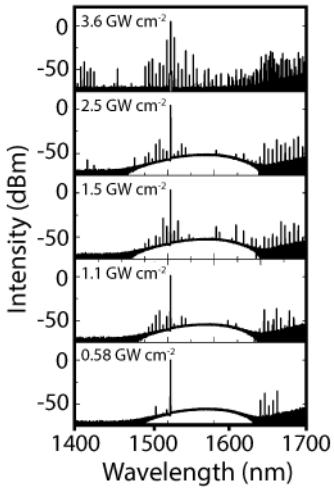

Fig S6. The comb generation in a resonator coated with CTAB-coated nanorods at a colloidal concentration of 0.125 mM.